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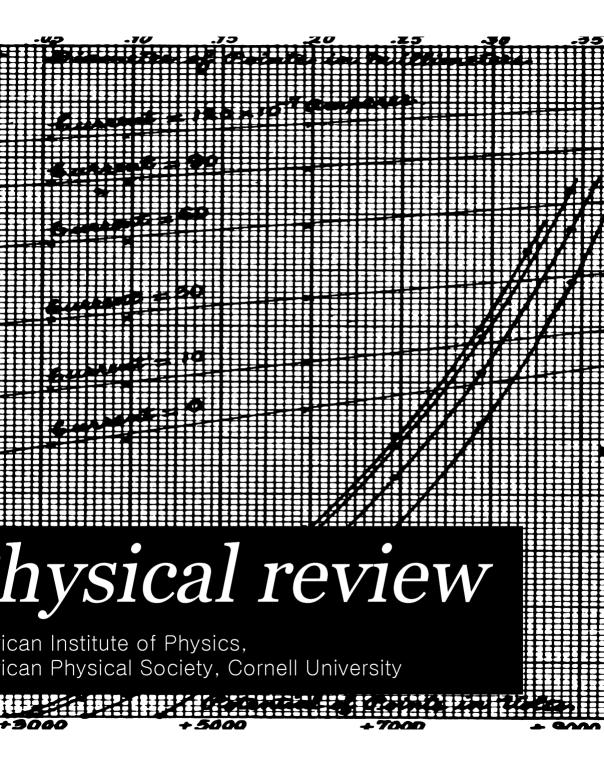
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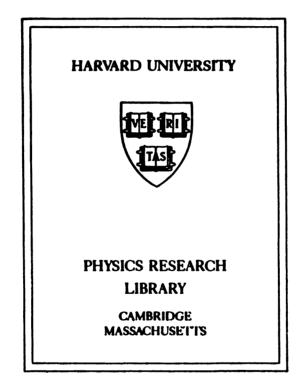
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# THE

# PHYSICAL REVIEW

A JOURNAL OF EXPERIMENTAL AND THEORETICAL PHYSICS

CONDUCTED WITH THE CO-OPERATION

OF THE

# AMERICAN PHYSICAL SOCIETY

BY

EDWARD L. NICHOLS, ERNEST MERRITT, AND FREDERICK BEDELL

Vol. XXVI



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### THE

# PHYSICAL REVIEW.

### CONDITIONS AFFECTING THE DISCHARGE OF ELEC-TRODES IN PHENOMENA OF IONIZATION.<sup>1</sup>

#### BY J. G. DAVIDSON.

IN the present paper is given a general outline of work that has been done at various intervals during the last two years. The original intention was to determine the influence of the temperature of the electrodes on ionization currents in flames, and to study the differences in phenomena when salts are ionized in flames and on hot metals. The results obtained in those fields led directly to some experiments in photo-electrical effects. Tables of readings are omitted because no new mathematical developments are investigated and the qualitative results are of chief importance. Only a few recent investigations are referred to, since full accounts of earlier researches are given in the standard works on ionization. Brief sketches of some of the writer's earlier results have previously been published.<sup>2</sup>

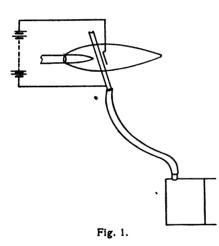
#### I. PHENOMENA OF FLAME CONDUCTIVITY.

### Effects of Position and Temperature of Electrodes.

I. Many of the most striking phenomena of flame conductivity were known long before the ionic theory was advanced. Those most nearly related to the present work are (I) that the area and position of the anode are of small importance, (2) that the current increases with the area of the cathode and as it is brought into the

hotter parts of the flame and (3) that the introduction of salts of the more electropositive metals, especially under the cathode, greatly increases the conductivity. It is easy to understand how such facts as these, combined with the phenomenon of the copious emission of negative ions by incandescent metals, led to the idea that the ionization takes place at the cathode and is due to its temperature. The theory of a "volume dissociation" was introduced about 1904<sup>1</sup> and is now generally accepted. For example, H. A. Wilson<sup>2</sup> estimates the average number of molecules that are ionized in a flame at one time.

2. Some experiments carried out by the writer in the autumn of 1905 furnished the first direct evidence as to the influence of the temperature of the electrodes on the current through a flame. Thin



metal tubes were used as electrodes: these could be kept quite cold by passing water from an insulated reservoir through them. When the water was shut off, all the conditions but the temperature of the electrode remained unchanged. Tests were made with tubes of aluminum, copper, brass, iron and platinum. In no case was the temperature of the anode found to have the slightest influence.

One special exception was discovered later and is recorded below (I., 15).

3. In a colorless flame, a cold cathode was unexpectedly found to give, within one per cent. as great a current as was obtained when the water was shut off and the tube raised to brilliant incandescence. Galvanometer deflections of 20 divisions with white hot tubes were reduced in every case by a fraction of a division too small to read on cooling the tubes (one galvanometer division

> <sup>1</sup> Marx, Phys. Zeit., 5, 298, 1904. <sup>2</sup> H. A. Wilson, Proc. Phys. Soc. Lond., 20, 147, 1906.



=  $1.4 \times 10^{-6}$  amperes in all the experiments recorded). If a platinum cathode is being used, great care must be taken to have it entirely freed from all traces of absorbed salts. The importance of this will appear throughout the paper. The experiments proved quite conclusively that the electrons which any of the above given metals emit at white heat and the secondary ions which may be produced by them in the flame in fields as great as 1,000 volts cm. are not sufficient in number to be comparable with the volume dissociation of the flame gases, due to temperature alone.

4. Slightly different results are obtained when the flame is colored by alkaline salts. In such salt flames the current increases decidedly when the cathode is allowed to become incandescent. With copper, iron, brass and aluminum the increase is small, amounting to between two and three per cent. when the flame is densely colored, while with platinum the current may be doubled. Typical readings in densely colored flames are:

Copper tube, cold, 400 div.; white hot, 410 div.

Platinum tube, cold, 320 div.; hot, 600 div.

If a platinum tube as cathode is kept cold for a time in a densely colored flame and then allowed to become suddenly white hot, the current will increase for a few seconds to two or three times its steady value. Now it is known that currents amounting to several amperes per sq. cm. may be obtained from platinum cathodes thoroughly coated with alkaline salt and heated in a strong flame. Α platinum wire held in a dense salt flame and then introduced into a clear flame will color it for a short time, and while this lasts a large current can be obtained, if the wire is the cathode. Thus in the salt flames there is a steady amount of salt absorbed or occluded in the platinum cathode. As this is ionized, the cathode can take advantage of every positive ion set free within itself. When it is shown below (I., 7-11) that a cathode can gather positive salt ione from only a short distance about itself, the effect of the temperaturs of a platinum cathode is explained.

5. Although it is thus proved that the greater part of the con-

Thomson<sup>1</sup> says : "Ionization involves the separation of a positive from a negative charge of electricity; if these charges are placed close to a metallic plate, other charges will be induced which will almost annul the attraction between the original charges." Several cases of some such assistance as this are recorded in this paper, especially in II., 8 and IV., 3, but, as platinum and palladium alone show the effects to any noticeable degree, it may be due rather to the absorptive and catalytic action of the metals. One example may be given here. A calcium salt sprayed into a flame causes a very slight increase in conductivity compared with that due to an alkaline salt. This harmonizes with our theory of line spectra, since the calcium lines barely appear in a flame spectrum, although the band spectrum, supposed to be due to undissociated molecules, Evidently very little calcium salt is ionized by the flame is strong. alone. If, however, the cathode is coated with either salt, the conductivities are enormously increased and approximately equal. With an alkaline coating the large current ceases when the coloration of the flame ceases but with an alkaline-earth it persists long. after. Coating the anode alone with a calcium salt gives no increase in conductivity even though the cathode is just above it in the ascending gases. Since, then, the calcium salt is ionized on the cathode but not on the anode nor in the flame itself, where the temperature is the same, the metal must assist in separating the ions and in setting free the negative but not the positive. Wehnelt<sup>2</sup> has studied this emission of negative ions from calcium salts and shown that they are electrons at low presuress.

#### Influence of Position of Cathode in Colorless Flame.

6. It has long been known that, as the cathode is brought into the hotter parts of the flame, the current gradually increases, but no one seems to have noticed the following phenomenon before it was recorded in the writer's first paper. If a strong enough air blast is used to give a sharply-defined green cone and the cathode introduced into this, the current will be from ten to twenty times as great as can be obtained with it a millimeter away but outside the cone:

> <sup>1</sup> J. J. Thomson, Cond. through Gases, p. 174. <sup>2</sup> Wehnelt, Ann. d. Phys., 14, 425, 1904.



this is altogether out of proportion to the difference in temperature. This large current is barely decreased by cooling the cathode with water as described above, nor does it show any approach to saturation with the greatest electric fields available. Again, if the cathode outside the cone is further heated electrically, the conductivity of the flame is increased considerably, but even with the platinum melting it is not nearly so great as in the cone. Examples of readings are : platinum cathode, just outside cone, 15 div.; in the cone, 200 div.; 5 cm. above cone, but in the flame and melted by a heating current, 90 div. Thus the cathode must be in the region of greatest ionization to give the greatest current, but the fact that in these positions its temperature is highest is an incidental and not the determining factor, unless it is coated with salt.

#### Velocity of Positive Ions in a Flame.

7. There has been a serious discordance of results in the researches on this point. The importance of the problem demands that some agreement should be reached. Wilson <sup>1</sup> placed the anode above the cathode, held a salt bead between them in such a manner that the colored vapor would not touch the cathode, and noticed the E.M.F. at which the current began to increase. Knowing the upward velocity of the flame gases, this gave at once, for the specific velocity of the positive ions, 62 cm./sec. With high E.M.F. he actually obtained greater currents with the anode above than with the cathode in the salt vapor. The writer has entirely failed to reproduce any such result, even a field of over 1,200 volts/cm. being insufficient to draw positive ions downward or outward from the colored vapor against the current of gas in any flame.

8. Moreau<sup>2</sup> placed the electrodes parallel and opposite each other, the cathode being in a colorless part of the flame. At the voltage at which the current begins to increase, it is assumed that the ions move from the salt vapor about the bottom of the anode to the top of the cathode diagonally. Now, the currents obtained in this way are of approximately the same magnitude if the salt is taken away entirely. I can see no reason whatever for assuming

> <sup>1</sup> H. A. Wilson, Phil. Trans., A., 192, 499, 1899. <sup>2</sup> Moreau, Ann. d. Chem. et d. Phys., 30, 33, 1903.



that the cathode gets its positive ions from the salt vapor rather than from the clear flame about itself.

9. Marx,<sup>1</sup> from a study of the potential gradient near the electrodes, deduced a value of 200 cm./sec. for the velocity of the positive ions. The validity of the method of measuring potentials in ionized gases by exploring electrodes is discussed below (I, 17).

10. Lenard<sup>2</sup> showed that the colored part of the flame is slightly deflected in a strong electric field in a direction indicating that it bears a positive charge. From his results he deduced a velocity of only .08 cm./sec. for the positive ions of lithium. This value was verified by the writer as to order of magnitude, but it varies, becoming smaller in more densely colored flames. Two confirmatory tests were also devised. An arc was started at various points in a colorless flame through which a current was passing between platinum electrodes. No increase was obtained until the arc was almost directly below the cathode, when the current became as large as in a small flame. Positive ions from metals which are not ionized in the flame were proved in this way to have very small velocities similar to those from alkaline salts. Again, a salt bead, which did not color the flame very densely, was held so that the colored vapor just surrounded the cathode, and no increase of current was obtained by using other beads to color the whole region between the electrodes.

11. It would seem proved that the positive ions which actually reach the cathode from the salt vapor in the flame come from a very thin layer surrounding it, and that most of the work on their velocities has been based on the misapprehension that they may be attracted to the cathode from salt vapor at a considerable distance.

12. No effort was made by the writer to find the velocity of the positive ions in a colorless flame, but it cannot be nearly so small as that of the salt ions, since in a moderately hot flame currents

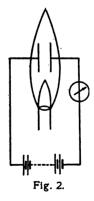
#### No. 1.] DISCHARGE OF ELECTRODES IN IONIZATION.

13. Assuming, in accordance with the kinetic theory of gases, that viscosity may be neglected and that velocity vanishes at each collision, a simple calculation<sup>1</sup> gives about 10 cm./sec. as the specific velocity of an atom of sodium bearing ionic charge in a gas at atmospheric pressure and  $2,000^{\circ}$  C. Many recent investigations show that an ion outside the flame soon gathers many thousand molecules about itself. This tendency must be present in the flame, though the aggregates may be broken up almost as soon as formed. Hence the viscosity factor may be sufficient to reduce the velocities to the observed values which are of the same order of magnitude as those found by Professor Lewis<sup>2</sup> for the positive ions just above the flame.

#### Source of the Negative Ions that Reach the Anode.

14. Different convection methods have been used for finding the velocity of negative ions in a flame. In every case it is assumed that, at the "critical voltage," the field is just able to draw the ion from the cathode or from the colored part of the flame to the upper edge of the anode before it is carried away by the gas currents. The inaccuracy of this conception can be proved experimentally as follows: With apparatus arranged as in Fig. 2, almost exactly the

same current-voltage curves and the same critical voltage were obtained when the anode was lowered or removed to a greater distance, while the cathode remained fixed; though the field, of necessity, changed. When several flames were arranged to touch only at tips and bases, the anode could be moved to any position with only a few per cent. change in current, and a large increase was noted only when the area of the electrodes was great compared with the distance between them. Again, it was interesting to use exploring electrodes, connected through a galvanometer with no voltage



applied, in a colored flame through which a large current was passing between two other electrodes. With one exploring elec-

<sup>1</sup> J. J. Thomson, Cond. through Gases, p. 203. <sup>2</sup> E. P. Lewis, PHYS. REV., 21, 352, 1905.



trode in any relative position near each of the main ones, considerable currents could be tapped off. If the exploring electrodes were placed symmetrically above the main anode, the one with the greater area became the anode for the galvanometer circuit and conversely with the cathode.

15. Mention has been made of the great increase in current obtained by coating the cathode with salt instead of spraying it into the flame. Using small voltages, it was not found possible to increase the current by coating the anode also or by holding it in the colored flame above the cathode. However, as the voltage increased the advantage did appear and increase, until with several hundred volts it often amounted to ten per cent. Coating the anode with an alkaline-earth salt is never of any service, because no positive ions can be emitted from it. Again, a large current was obtained by coating the cathode with a salt; only a very slight decrease in current was noticed when the anode was removed to the base of an intense flame inclined to the first and touching it only at the tip. The current decreased rapidly as the second flame was made less intense, but coating the anode with an alkaline salt brought it back to its former value in every case. An exploring electrode took up positive potentials in the anode flame, negative in the cathode flame, and became neutral at the tip where the flames mingled, thus showing that above the anode there was a large excess of positive ions and an excess of negative above the cathode, the two neutralizing where the flames joined. This is like the case of an ordinary flame with the part between the electrodes cut out. Its absence makes little difference in the current, as we have seen. Now, with both electrodes in our flame and opposite each other, an exploring wire reveals a similar state above the electrodes, as in the case of two flames : there is always a part of the intervening space where a uniform fall of the potential shows equal densities of positive and negative ions.

16. It has already been shown (pars. 10 and 11) that the cathode gets its positive ions from only a very thin surrounding layer. Many experiments like the examples just given (pars. 15 and 16) have led me to believe that the anode gets enough negative ions from the clear flame about itself, even when the cathode is in salt

#### No. 1.] DISCHARGE OF ELECTRODES IN IONIZATION.

vapor and quite large currents are passing. This means that the remaining negative ions about the cathode and positive ions about the anode unite between the electrodes, and especially in the upper regions of the flame. If this conception of the action be correct, it invalidates any method as yet employed for finding directly the velocity of the negative ions, because a state of steady drift of negative ions from cathode to anode is assumed in each case.

#### Potential Gradient.

17. The method of finding potential gradient in regions of ionization by means of an exploring electrode has been attacked on the ground that when a wire takes up a potential it distorts the field. However, if the area of the wire is small as compared with that of the electrodes, the distortion can hardly be great enough to change the character of the results. But I would suggest more valid objections to the deductions that are ordinarily made from potential gradients found in this way. If the potential of the wire were any measure of the actual space potential, it would be proportional only to the relative numbers of positive and negative ions at that point. A little thought will convince us that it depends on their mass and velocity as well. Suppose the wire takes up a negative potential. A certain number of negative ions, depending on their density and momentum, will still strike it in spite of the repulsion, while its steady state will be maintained by an equal number of positive ions, depending, again, on density, mass and velocity, but assisted by attraction. In the published researches on the problem, the assumption is tacitly made that the potential gradient indicated by the wire and the ionic velocity are functions only of each other, thus ignoring the question of relative density and mass.

18. I have not as yet had the opportunity of gathering data for attacking the problem from this broader standpoint. However, during the course of the experiments, a number of series of measurements was made in which current, position of electrodes and socalled potential gradient were varied so widely as to give velocities varying from 500 to 10,000 cm./sec. if the usual assumptions were made in the calculation. There seemed no particular evidence that any one value was more nearly correct than another.

1,000 cm./sec. has hitherto been the most widely accepted value. Recently Gold<sup>1</sup> has obtained 12,900 cm./sec. by using the convection method and finding the potential gradient in the body of the flame. Calculation gives 13,000 cm./sec. for an electron, assuming no viscosity.

II. IONIZATION OF SALTS ON HOT METALS.

I. The experiments described in this section were undertaken in order to ascertain the variation of phenomena in ionization of salts when freed from possible effects of the chemical actions of the flame. Many of the results obtained have recently been published by others but some new facts are still to be recorded and some general relations to be pointed out.

2. J. J. Thomson<sup>3</sup> heated various salts to a red heat and measured the excess of electricity of either sign in the surrounding air by means of an electroscope. The sign depends on the salt, not on the metal. Oxides give excess of negative; phosphates a large and chlorides a small positive excess; nitrates give initial positive excess, but they soon turn to oxides. The salts remain with the opposite charge. He suggests in explanation that the salts have a double layer of electricity, the oxides having negative outside. Garret<sup>3</sup> placed the salts in a platinum dish in a metal tube and heated them by insulated gas flames. The tube was one electrode and a wire along its axis the other. He used temperatures only as high as  $360^{\circ}$  and, naturally, got no general idea as to the action of different classes of salts. For example, he got neither positive nor negative ions from KBr, NaFl, NaHCO<sub>3</sub> and Ba(NO<sub>3</sub>)<sub>2</sub>. None that he tried gave negative ions only, while a few gave positive only.

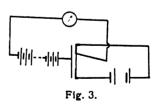
3. I add the following observations: The other haloid and the sulphur salts, the hydroxides, and higher oxides, while changing to lower, also show initial excess of positive ions, as do the alkaline oxides alone among those tested. But none of these is permanent; ultimately an excess of negative ions always appears in the sur-

bromides of calcium, strontium and barium but the sulphates are more permanent and require a higher temperature. In most other cases it takes long-continued heating of a very small quantity of the salt at a high temperature to affect it. It would seem that all salts ultimately break down into oxides and that chemical actions, which leave the metal behind and give off other products, give excess of positive electricity in the air. In those cases where negative ions alone are being given off, there is no reason to believe that any chemical action or volatilization is taking place. The same salt of different metals requires widely different temperatures to effect ionization. In general, the alkaline salts are most easily ionized. I detected ions from KNO<sub>3</sub> at 250° and from RbCl at still lower temperatures. Campbell has even found them at room temperatures.

4. To study the intense ionization of certain salts at high temperatures, they were placed on pieces of platinum wire 2 or 3 cm. long, heated electrically and earthed. The other electrode was a plate or wire whose distance from the hot wire could be adjusted. A battery of small accumulator cells gave adjustable E.M.F. to 550 volts. A d'Arsonval galvanometer of approximately 375 ohms resistance and giving a deflection of one scale division for  $1.4 \times 10^{-6}$  amp. indicated the currents. It was not sensitive enough to reveal the ionization of most salts.

5. Any salt of an alkaline-earth metal will give a current of four or five divisions with the hot wire as anode and slightly less with it as

cathode, as long as volatilization is taking place. Then there is no sign of an anode current even with the cold cathode attached to an electrometer, while with the hot wire as cathode, the galvanometer deflection is as high as 500 divisions with 480 volts and 2 mm. between the elec-



trodes. At white heat this current is about the same for all the salts of the same metal. This was attributed above (par. 3) to their all breaking down into oxides. Barium salts give the largest currents of the group, magnesium and zinc the least. Comparative readings under circumstances as nearly as possible similar, were, for instance : Barium, 600 divisions; strontium, 550; calcium, 500;

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magnesium, 20; zinc, 30. An electrometer had to be used to detect the emission of the negative ions from beryllium salts.

6. With coatings of alkaline salts also, these large currents were obtained when the wire was hot enough to volatilize the salt. In most cases a dull red heat was sufficient. The currents were never persistent, disappearing as volatilization ceases. With these salts, deflections of not more than one division could be obtained with the hot wire as cathode, but with it as anode 400 or 500 divisions could easily be obtained. Every alkaline salt of the thirty or more that were used gave a similar result, though some were more persistent and needed a brighter red heat than others. Rubidium and cæsium gave the largest currents of the group and lithium the least.

7. A great many salts of metals in every group of elements were examined to find if these large currents could be obtained. The wire was gradually raised to brilliant incandescence in each case; a much higher temperature than is necessary for the ordinary emission of negative ions. Brief and comparatively small anode currents of from one to four divisions were obtained from many salts, especially those of metals of large atomic weights, in all the groups. Some of them may be due to very slight traces of alkaline impurity as the currents died away while the salt was still volatilizing. Alone, of all the salts tried, except those of alkaline-earths, didymium nitrate gave a cathode current of one division and molybdenum oxide 3 divisions. These may also be due to impurities.

It is remarkable that this emission of positive ions from alkaline salts was not recorded earlier, as the property is so very marked.

#### Effect of the Metal of the Wire.

8. Wires of platinum and palladium, alone, were found by the writer to give these large ionization currents: the latter is the more effective. Wires of german silver coated with CaO were found to give a cathode current barely large enough to affect the galvanom-

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I have found is alternately to dip the wire in acid and place it as an electrode in a flame with large voltage applied, making it anode or cathode according as the absorbed material is alkali or alkalineearth.

#### Action of New Wires.

9. It is known that a new platinum wire will give a large leak of positive ions at red heat, and that the current soon falls to a small steady value. Richardson has done a great deal of work on this subject and has practically concluded that the leak is due to occluded hydrogen. There is, apparently, no evidence for this other than that hydrogen diffusing outward through an anode increases the positive leak. To my mind there can be no doubt that it is due to alkaline salts. These placed on a clean wire will give the effects obtained from a new wire, and any new wire will give the sodium color to a flame. Some photo-electric phenomena described later in the paper (IV., pars. 5, II and I3) practically settle the question.

#### The Anomalous Action of Alkaline Salts.

10. It has been seen that coating an anode in a flame with an alkaline salt gives no increase in current if the cathode is clean and kept in the colorless part of the flame while, from alkali-coated cathodes currents, of several amperes per sq. mm. can easily be obtained. In air, on the other hand, an incandescent alkali-coated wire gives by far the largest currents when it is the anode; for example, in one case, with 250 volts between electrodes 2 mm. apart a platinum wire 3 cm. long, coated with NaHCO, gave negative leaks of  $4 \times 10^{-7}$  amperes and positive leaks of  $2 \times 10^{-5}$ amperes when it was anode. The anomaly has been partially explained already (I., pars. 7 and 11). It has been seen that, in the flame the positive ions accompany, and probably constitute, the colored portion. Owing to their low velocity they are swept away in the flame gases so that the cathode must be placed in the salt vapor to obtain any greater current than that due to the colorless flame. Similarly it was found that a very slight blast of air will sweep away the positive ions and stop the large current from a hot alkali-coated anode in air.

The explanation of the very small negative leak from the hot alkali-coated cathode in air finally appeared in some modifications of Owens' experiment. He showed that a current of negative ions is stopped by blowing smoke between the electrodes: the ions appear to attach themselves to the smoke particles and be carried away. I noticed that the large negative leak due to a calcium salt on a hot cathode in air does not commence while any fumes are being given off. With alkaline salts there is volatilization as long as any current of either sign will pass. If the wire is cathode the small current is actually increased by a slight blast of air, if the temperature is kept constant, but it is entirely checked by smoke. On the other hand, dense smoke does not decrease the large positive leak in the slightest degree; either the positive ions have momentum enough, owing to their large mass, to carry the smoke particles to the cathode with them or they do not attach themselves to those particles nearly so rapidly as the negative ions. The volatile salt vapor acts the part of smoke sufficiently to make the negative leak from alkali-coated wires in air very small in comparison with the positive leak.

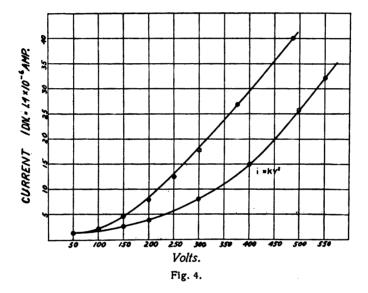
#### Relation between Current and Temperature.

12. Richardson's formula<sup>1</sup> is now generally accepted. Where i is the current,  $\theta$  the absolute temperature and a and b constants,  $i = a\theta^{\frac{1}{2}}e^{-b/\theta}$ . The formula has been rigorously tested in a great many cases with currents of both positive and negative ions and gives fair agreement with experimental curves in all cases where the current is maintaining a steady value at any constant temperature; that is, where the rate of volatilization of the material ionized is comparatively small. I mention the matter in order to point out that the formula was first developed for negative leaks and that the theory from which it was derived is based on the assumption that electrons are circulating in the metal like molecules in a perfect gas. This, of course, does not apply to positive ions and a new basis for this formula or a new formula giving curves of similar shape, must be devised.

<sup>1</sup>J. J. Thomson, Cond. through Gases, p. 166.

#### Relation between Current and Potential Difference.

13. The formula<sup>1</sup>  $i = 9Rv^2/32\pi d^3$  is widely used for cases where the ionization is confined to a thin layer near one electrode. The writer has tested it for ionization of salts on hot wires and has found that the experimental curves depart widely from the calculated values. As an example, the diagram (Fig. 4) gives the currentvoltage curve for an incandescent wire cathode, 3 cm. long, coated with CaO and about 2 mm. from the anode. When, however, the



voltage is kept constant and the distance between electrodes varied, the experimental curve is found to be considerably below the theoretical. One reason for this is that the velocity R varies with both the potential difference V and the distance between the electrodes d, since the ions increase in size with the time. The rate of variation of R with time and distance might be determined were it not for another difficulty. It is assumed in the development that, if the current is small, the potential gradient vanishes at the hot plate. An exploring electrode certainly indicates that this is true, but, as stated above, it can hardly be supposed to give the true potential of the space, and under any circumstances, one can hardly conceive of

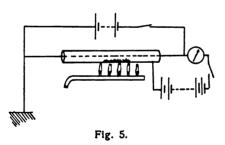
<sup>1</sup> J. J. Thomson, Cond. through Gases, p. 175.

there being enough ions near the hot plate to prevent any fall of space-potential.

III. IONIC AGGREGATES AND APPARENT RECOMBINATION.

1. Ions formed in dry, dust-free gases at ordinary pressures by such ionizing agents as X-rays, radio-active substances or ultraviolet light, never seem to collect aggregates of molecules about themselves. Those escaping from flames or hot metals are much larger and they grow still larger and more sluggish the farther they are removed from the source and the lower the temperature becomes. The calculated values of their size have been steadily increasing until Langevin<sup>1</sup> in the latest paper on the subject gives an average of 64,000 molecules.

2. In many places in the work of Barus, it is shown that nucleation does not disappear with recombination of ions. In some preliminary tests on ionizations of salts the writer used the arrangements



of Fig. 5. If both wire and tube were kept hot for a time before the galvanometer circuit was closed, a considerable initial current and then a much smaller steady one was obtained. Both initial and steady currents were very much larger than when the heating

circuit was opened just before the galvanometer circuit was closed. This first suggested to the writer the following conception of the action. When two ions of opposite sign, consisting each of a charged particle surrounded with layers of molecules, come together, the combination will be neutral electrically, but molecules may still remain between the charges. In cases of such apparent recombination the field between the positive and the negative particles will be much weaker than in cases of genuine recombination. This

#### No. I.] DISCHARGE OF ELECTRODES IN IONIZATION.

positive, negative or zero. If this view is correct, some of these aggregates should be capable of collection on a charged wire and then be more easily re-ionized than before. The experiments described in the remainder of this paper were all directly suggested by this conception. It can hardly be said to be proved, but at any rate, it has already been fruitful of results.

3. Flame gases were led through a metal tube in which was a central insulated electrode, consisting of about 3 cm. of platinum wire attached to larger supporting copper wires insulated from the tube. The central wire was kept charged in the gases to make the collections. The flame was then removed and the wire heated electrically.

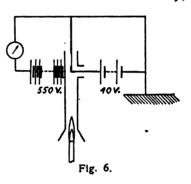
while cathode or anode, to obtain an ionization current, the tube being the other electrode. In all cases the currents were about equal, whether the wire had been charged positively or negatively during collection.

If an uncolored flame had been used, very slight and brief currents that could just be detected by the galvanometer were obtained.

to drive off all the collected material.

When the flame was colored by salt vapors currents were obtained like those described in the previous section and the large effects appeared at decidedly lower temperatures. In fact, it was in this way that the large positive leak from hot alkali-coated wires was first discovered. When the flame was colored by an alkaline-earth salt the wire had, of course, to be the cathode when heated to give a current. Small quantities of material will collect on an uncharged wire above a sodium flame, but practically none above a calcium flame. The currents obtained in this way are so large as to be of a different order of magnitude from the steady currents obtained between the tube and a cool central electrode while the flame gases are rising.

4. These collections furnish an extremely delicate test for the presence of minute quantities of such salts suspended in a gas that



A dull red heat was sufficient

has been exposed to any ionizing influence. Professor Rutherford, while at this university in the summer of 1906, kindly gave the writer some radium emanation for a test. A charged wire in a dry vessel containing the emanation collected no such deposit as those here discussed. When the vessel was dampened with distilled water I detected a very slight anode current when the wire was discharged, removed and heated. After tap water was poured into the vessel and shaken up, a wire charged to 500 volts would collect enough in two or three minutes to give a large but very brief anode current of 10 scale divisions with the wire at a dull red heat.

5. Anode currents, presumably due to minute traces of alkaline material, were obtained from wires that had remained charged in freshly-prepared gases, or in the air of the room, especially if it circulated past the wire. On days when the north wind was blowing enough would collect on a wire in a field of 500 volts/cm. in one minute to give 25 divisions of scale deflection, while on other days whena west wind was blowing not more than 1.5 divisions could be obtained under circumstances otherwise similar. Mr. F. A. Harvey, working in this laboratory, found abnormally large quantities of radio-activity in the air on the same days when a north wind was blowing, and there may yet prove to be some connection between the phenomena.

6. Something always collects, from the gases tested, on an uncharged wire. This could easily be extracted by passing the gas through long tubes of water or plugs of cotton wool, but some material which could be collected on a charged wire still remained in the gas in every case. Potentials approaching sparking values and very slow currents of gas must be used in order to collect as much as possible.

#### The Nature of the Collections.

7. For a long time it seemed that these collections might be due to purely electrostatic attraction of neutral particles and that there was no necessity for assuming any resultant charge on the aggregates. Evidence on the subject was given by an examination of the cold electrode when salts were heated on a neighboring one. When a salt that sublimes or volatilizes readily is used, the smoke is all



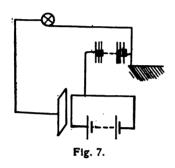
deflected to the cold electrode and forms a white deposit. With salts, like those of the alkali metals, that cause either a positive or a negative leak, the direction of the field causes comparatively little change in the rate of collection and the appearance of the deposit. Silver and thallium nitrates were found to give only a positive leak while volatilizing strongly, and with these the deposit formed much more rapidly with the hot wire as anode.

8. This theory of ionic aggregates suggests at once a simple explanation of the so-called "double layer" that occupies such a large place in the history of this subject. The aggregates may not allow the charged particle to reach the metal and, if so, a bound electrostatic charge will be induced on the surface. Thus it ought to be possible to obtain a kind of electrolytic polarization on a charged cold electrode, in a space where such ions are plentiful. In 1800 J. J. Thomson made the isolated observation that in certain cases an ionization current from a hot metal was increased when the other electrode was heated also. I investigated the question somewhat, as it seemed to bear on this point. When an alkaline-earth salt was heated on the cathode, heating the anode also did not increase the current if the wire was absolutely clean at the start. Very few aggregates appear in the air space in this case. When an alkaline salt was used there was a large increase when the second electrode was heated, but most of this was proved to be due to the salt being volatilized back and forth between the electrodes. When, however, a very small anode was used and the cathode removed while the anode was heated after the current had passed for a time there was a brief but decided increase in the current. Whether this was due to a non-conducting layer of salt or a genuine double layer as described above, could not, of course, be determined.

#### IV. PHOTO-ELECTRIC PHENOMENA.

I. In following out the ideas of the previous section, I undertook to find whether a wire held in regions of ionization will gather material upon its surface which can then be easily re-ionized by ultra-violet light. The investigation has led to a variety of important results, many of which are not connected with any theory of ionic aggregates except that they were suggested by experiments in that direction. ł

2. For measuring the negative leak under the influence of the ultra-violet light at room temperatures an encased electroscope was used in a part of the work. The wire to be tested was attached to the leaf support and projected beyond the case. This method gave the character of the results very expeditiously. For more accurate work and for high temperature effects a quadrant electrometer enclosed in a metal box was used. Covered wires connected one



pair of quadrants to a strip of corroded metal plate or gauze placed near the active wire or polished metal being tested. Shielding was practically unnecessary, as even with the electrometer electrode at a high negative potential there was practically no leak due to the light. Both pairs of quadrants were earthed at the beginning of each reading. The wire being tested could be

heated electrically and was kept at a high negative potential by connection with a storage battery giving a maximum of 100 volts. Hence, the rate of leak to the electrometer electrode measured the effect. An arc was used as source of light in most of the work. It is far more easily handled than a spark source and with a little practice can be made quite constant.

#### Wires Exposed to Flame Gases.

3. New platinum or palladium wires show very little activity; cleaned as indicated below, they show practically none. After being held in a colorless flame, however, they were found to be very active. Where, for example, such a wire gave 100 divisions of electrometer leak per minute when charged negatively and exposed to strong ultra-violet light, a strip of brightly polished zinc of approximately the same area gave no more than 40 divisions. Observations on wires held at various distances above a flame showed that the effect still exists but that it falls off rapidly. Passing a wire rapidly once or twice through the gases just above the flame, so that its temperature had no time to rise materially, made it more active than holding it for a minute at the top of a tube 2 meters



long through which all the gases from the flame were rising. Hence the gases, after leaving the flame, rapidly lose their power of making the wire sensitive. Charging the wire either positively or negatively while in the gas did not seem to hasten its gaining of sensitiveness. Ultra-violet light was admitted at various intervals through a quartz window into a tube through which flame gases were rising and into a large vessel filled with the gas, and only a very slight increase in ionization was observed. However, the wire will retain its activity most persistently; here again is an example of the effect of a metal in promoting ionization at its surface, spoken of above (I., par. 5). When wires were left in the open air their activity fell off gradually to half value in two or three days, but this seemed to be due to the formation of a layer of dust particles. After a wire had been kept covered in a bottle for a week the intensity of its activity was as great as at first but it would not maintain the discharge nearly so long. Wires that had been held in the flame maintained a constant discharge in a constant field for as much as two hours, and then the leak dropped to zero in two minutes. They did not recover their activity spontaneously. The activity gathered on wires held above the flame at various heights becomes rapidly less persistent as the distance increases; for example, a wire which had been held 10 cm, above a flame for 10 sec. maintained a steady leak of 40 divisions per minute for an hour before the rapid decrease in activity commenced, while, after being at the top of the tube 2 meters long for the same time, it gave 5 divisions per minute for 10 minutes; intermediate positions gave intermediate readings. In passing, I might remark that no one seems to have stated definitely that all the well-known cases of photo-electric "fatigue" are functions of the strength of the field.

4. Coloring the flame with an alkaline salt decreases the effect : in fact, when a charged wire was held for a minute above a dense salt flame it showed only a slight initial activity. The ionic aggregates from salt vapors, discussed in the previous section, are not, then, re-ionized by ultra-violet light. Oxidized or corroded pieces of metal were found to be slightly active after being held for an instant above a clear flame.

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#### Electrodes from Electrolytic Cells.

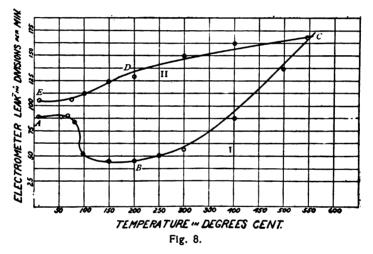
5. With one exception, (given in par. 6) platinum wires that had been either cathode or anode in electrolytic cells of many kinds were found to be very active after being allowed to dry. A wire at which hydrogen had been liberated behaved like a wire from a colorless flame when tested at room temperatures. Various metals were deposited on wires and all showed the effect strongly, but for metals of the first two groups the current through the electrolyte must be very brief or the wire becomes saturated with the hydroxide which is not sensitive at low temperatures. The activity of all metals in these tests falls off with the time and is not recovered. Anodes in solutions of halogen salts also become active but the decay was not investigated. In all cases currents of several amperes through the electrolyte are advisable; it would seem that some ions have not time to become neutralized and that these are later set free by the light.

6. It was found that oxygen set free electrolytically at a wire would not make it active and would even destroy any activity which it may have possessed. However, really to clean the wire it is well alternately to dip it in acid and heat it in a flame to get rid of all metallic salts, before making it an anode in the cell, or the oxygen may leave it saturated with insoluble oxide. The discovery of this method of cleaning a wire made the whole investigation practicable. It was only after a great deal of experimenting that I realized what extreme care must be taken in cleaning the wires to get reliable results.

7. Such a clean wire, after being heated to a red heat by an electric current, is found to be active at room temperatures. This shows that the effect of the flame gases is not necessarily due to occluded hydrogen as one is likely at first to suspect. Heating to white heat by an electric current does not decrease the activity of a wire newly heated in a flame. When, however, such a wire had

obtained temperature-activity curves for platinum and iron wires and attributed his results to the properties of the metals themselves. This conclusion, as will be seen, is not justified. Millikan and Winchester<sup>1</sup> have studied the photo-electric activity of metals at different temperatures in the highest vacua obtainable and have found no variation. Whether temperatures giving red heat were used is not stated in the published abstract of their work. My experiments and those of Zeleny were all carried out in air at atmospheric pressure when oxidation effects are important.

9. Only a single curve will be given (Fig. 8, one very similar to Zeleny's) that was obtained from a new platinum wire that had



been heated electrically once to a bright red heat and then was taken over the scale of temperatures again.

Curve I. is for increasing and Curve II. for decreasing temperature. It will answer every purpose to describe briefly a few of the curves actually obtained by references to the lettered points on the figure.

10. In many cases temperatures were reached at which negative ions due to the temperature alone began to cross in the dark from the wire being tested to the electrometer electrodes. The two influences were found to be practically additive; extending the curves due to light alone at lower temperatures and adding the ionizations in the dark gave the experimental curves.

<sup>1</sup> Millikan and Winchester, PHvs. Rev., 24, 116, 1907.

11. New wires showed no more than one or two divisions of leak per minute at 15°. This increased each time as the wire was raised to successively higher temperatures, and persisted for different periods with different wires, when the heating current was broken. Not until almost 400° had once been reached did the hysteresis effect with falling temperatures and the minimum from 100° to 300° with rising temperatures begin to appear. Then curves similar to those in the figure were obtained with each wire. The hysteresis is never an invariable phenomenon. If readings are taken slowly enough Curve II. retraces Curve I.; or we may stop at any point D on Curve II. and, by keeping temperature, field and light steady, gradually drop the activity to the corresponding point on Curve I., though it may take half an hour to do it. The point E never coincides with A unless the wire has been taken over the same or a higher scale of temperatures a short time previously.

12. A clean wire coated with any one of various alkaline salts that were tried gives a similar succession of results and, ultimately, curves of the same shape as the new wire, though the activities were quite different with different salts. This is considered a final proof that the occluded material in new wires is not hydrogen but alkaline salts.

13. A wire, cleaned as anode in an electrolytic cell, shows no activity until its temperature is raised to  $400^{\circ}$ , when it increases very rapidly. One wire gave 90 divisions of leak per minute at bright red heat and this included a slight ionization due to heat alone.

Dropped back to  $15^{\circ}$ , it gave 120 divisions. Then for rising temperatures, the drop in the curve appears at  $80^{\circ}$  as in the figure, but the minimum part *B*, reaching just to red heat was only 4-7 divisions. No hysteresis was observed unless the temperature is very rapidly lowered. This action of the clean wire must be due to occluded oxygen; it is certainly not a property of the platinum itself.

A clean wire that has been held in a flame gives results similar to those above, except that the point C is decidely higher; in 'oth cases it is lower than A until the wire is raised to white heat. A wire at which hydrogen has been liberated electrolytically gives curves almost identical with those from a flame.

14. I think that the curves obtained from new wires and wires

coated with salts are the resultant of the action of the salt and that of the clean wire, the minimum being due to the clean wire and the great activity at red heats with hysteresis effects being more especially the properties of the salt. McLennan<sup>1</sup> observed that some salts of calcium and sodium will give off negative ions when exposed to X-rays or ultra-violet light at temperatures between 200° and  $300^\circ$ . As research in these lines progresses we shall doubtless be able to obtain clear relations between these ionization phenomena and the chemical dissociation constants of the salts.

15. Several copper and iron wires were tested until it was found that polishing with emery paper leaves impurities on the surface that influence the result at high temperatures. Brightening the surface by scraping with a knife avoids this error. The leak remains constant from these two metals as temperature is raised quite rapidly to about  $175^{\circ}$ . Fatigue, however, is hastened by raising the temperature. At about 300° the leak from a polished surface can be seen to decrease rapidly. This must be due to oxidation. Again, at bright red heat, any oxidized piece of copper or iron which is quite inactive at ordinary temperatures becomes very active and brief hysteresis can be observed if the temperature is rapidly lowered. This is probably connected with reduction of some of the oxide to the metal by the heat.

#### Methods of Polishing.

16. It was accidentally observed that violently stretching a piece of copper wire that was not brightly polished greatly increased its sensitiveness, but not beyond that of a brightly polished surface. Squeezing in a vice and twisting were found to serve the same purpose. Violently scraping or rasping surfaces of iron, aluminum or german silver gives from 10 per cent. to 20 per cent. greater sensitiveness than thorough polishing in a lathe with smooth emery paper. On the other hand, the smooth polishing of copper gives about 15 per cent. the greater effect. A bright surface of any one of these metals has about the same sensitiveness after about half



resented as the resultant of two exponential curves, one with a much greater time factor than the other. It would seem from the experiments of this paragraph, incomplete as they are, that the initial rapid decay is a function of the treatment to which the surface has recently been subjected.

17. In attempting to account for the fatigue of metals exposed to ultra-violet light, different investigators advocate different theories, oxidation, formation of layers of neutral gases, double layers of electricity or a kind of chemical change in the metal itself. No one of these would seem to account for all the new phenomena recorded in this section and probably each will prove to be the true explanation of particular cases.

There are numerous cases of direct contradiction in the published researches on ionization phenomena. It is to be hoped that this paper has pointed out some of the real causes of these discrepancies. In particular, the difficulties arising from alkaline salts should be emphasized; they are found on all surfaces exposed to the atmosphere and it is extremely difficult to detach every trace of them; some of them, at least, are slowly ionized at room temperatures and all of them at  $400^{\circ}$  and above.

The main phenomena discovered during the research are :

I. The temperature of the electrode has only a slight influence on conductivity of flames: the apparent exception to this in the case of a platinum cathode in a colored flame is due to occluded salts.

2. The conductivity of the green cone in a colorless Bunsen flame is comparable with that of a colored flame.

3. Large currents due to the attraction of positive ions against the drift of the flame gases cannot be obtained.

4. Very rapid but brief leaks of positive ions can be obtained from hot platinum wires coated with alkaline salts.

5. The occluded material in new platinum wires is shown to be mainly alkaline salts.

6. A current carried by positive ions is not stopped by smoke.

7. Collections of molecular aggregation apparently bearing electric charges can be made on charged wires from many ionized gases and then easily re-ionized.

8. Platinum wires which have been held in flame gases or used

as electrodes in electrolytic cells (except where oxygen is set free) become very sensitive to ultra-violet light.

9. The minimum in photo-electric sensitiveness of platinum wires at temperatures between 100° and 200° is traced to the action of occluded gases.

10. The initial rapid photo-electric fatigue of metals is connected with the method of polishing.

I am deeply grateful to Professor E. P. Lewis and the other members of the physics department for unfailing interest and generous assistance during my stay in this laboratory.

UNIVERSITY OF CALIFORNIA, August 16, 1907.

## ON THE DENSITY, ELECTRICAL CONDUCTIVITY AND VISCOSITY OF FUSED SALTS AND THEIR MIXTURES.

BY H. M. GOODWIN AND R. D. MAILEY.

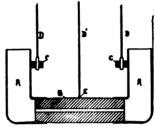
Contributions from the Research Laboratory of Physical Chemistry No. 16.

#### III. CONDUCTIVITY MEASUREMENTS.

THE conductivity of the fused salts was measured by means of the well known Kohlrausch method. The bridge was of the horizontal drum type made by Leeds and Northrup and consisted of 5 meters of manganine wire wound in 10 turns upon a marble cylinder. The wire was carefully calibrated by the method of Strouhal and Barus. The known resistance was a Hartmann & Braun standard resistance box calibrated to better than 1/20 per cent. An adjustable Swedish telephone was used for detecting the minimum, the alternating current being supplied by a small induction coil.

The novel and most important feature of the apparatus was the form of conductivity cell which we used. This was designed only after considerable experimenting with different materials and types of cell. The several properties which the material for a cell should possess if suitable for containing fused electrolytes at temperatures up to  $500^{\circ}$  C., are not readily found combined. The cell should be, first, a non-conductor of electricity at the highest temperature at which it is to be used; second, it should be chemically inert with respect to the substances contained in it; and, third, it should be of such a form that the actual ohmic resistance of the fused salt is fairly high, 100 ohms or over, on account of the very high specific conductance of these electrolytes. The form of the cell should also be such that large e ectrodes may be used in order to diminish the effect of polarization and consequent blurring of the minimum. A substance admirably fulfilling these conditions is quartz, either in the vitreous or natural crystalline form. The design of cell which we devised is shown in Fig. 6. B is a cylinder of rock crystal 5 cm. long and 14 mm. diameter, cut parallel to its axis, through which a capillary 1.5 mm. in diameter is bored with a diamond drill.

The ends are carefully ground to a slight taper. The ends of this cylinder are closed by platinum elbows A, carefully ground on with rotten stone, and these in turn form the two electrodes of the cell. They are so designed that the flow lines from the end of the capillary spread out over a large platinum surface thus reducing the effect of polarization to a mini-





mum. The cell is suspended in the furnace by means of platinum leads DD attached to the elbows by means of platinum plugs inserted in small platinum blocks CC.

It was originally intended to use fused quartz for this cylinder in order to eliminate the effect of temperature on the cell constant, but, owing to the large differential expansion between this substance and platinum, the cell invariably began to leak when the temperature was raised to 300° or 400° C. We therefore chose natural quartz crystal, as the coefficient of expansion of this substance at right angles to its axis happens fortunately to be very nearly that of platinum. The effect of the very slight leakage along the surface of Bwhich was sometimes observed at high temperatures, was corrected for by measuring, by means of an auxiliary platinum wire electrode DE, wound around the center of the cylinder, the resistance between this electrode and the two platinum ends. The correction for change of cell constant with the temperature could be accurately calculated as the expansion coefficients of quartz along both its axes are well known.<sup>1</sup> With this cell conductivities could be measured with a minimum as sharp as that obtained under best working conditions with aqueous solutions at ordinary temperatures. The precision of a measurement was practically determined therefore by the precision with which the true temperature could be measured.

<sup>1</sup>H. W. Randall, PHVS. REV., 20, pp. 10-37, 1905.

Another substance with which we experimented was pure magnesium oxide fused in the electric furnace. This substance is capable of being heated to nearly  $2,000^{\circ}$  C. before melting, is a fine insulator, and is chemically inert even at very high temperatures with respect to many neutral and alkaline compounds. The fused oxide is however, crystalline in structure and liable to contain blow holes which make it a difficult matter to obtain cylinders of sufficient homogeneity to serve as conductivity cells. For temperatures above which quartz cannot be used however, this substance offers great possibilities particularly as its coefficient of expansion is not greatly different from that of platinum.<sup>1</sup>

## DETERMINATION OF CELL CONSTANT.

To standardize the cell a solution of sulphuric acid was used, as recommended by Kohlrausch and Holborn,<sup>2</sup> and as a check on this, a saturated sodium chloride solution as well. The acid solution was made up from extra chemically pure sulphuric acid from Eimer and Amend by diluting it with best conductivity water until its density, as determined by an Ostwald picnometer, was 1.223 at 18° C. The saturated sodium chloride solution was made up by first heating to 80° C. an excess of purified salt with best conductivity water, then rotating this solution in a thermostat at 18° C. for four hours. The clear solution was then quickly filtered off by a special filtering apparatus. The process of filtration did not change the concentration appreciably, since a change of 29° C. would increase the solubility by an amount which would change the conductivity by only 0.1 per cent. The sodium chloride was prepared by precipitating it from a saturated solution of C.P. salt by hydrochloric acid gas, the precipitated salt being then dried in a platinum dish over a Bunsen burner.

The cell constant was determined at  $18^{\circ}$  C. in a felt jacketed thermostat filled with xylene. The thermostat was provided with

ured by a thermometer graduated directly in tenths of a degree the corrections of which were determined by comparison with the laboratory standard (Toneleau) which had been tested at the U. S. Bureau of Standards. As xylene is a good insulator, the conductivity cell was suspended directly in the bath.

The procedure in determining the cell constant was as follows: After connecting the cell into the bridge circuit it was washed out a number of times with the calibrating solution, then filled to within a few millimeters of the top of the elbows, and suspended in the xylene bath, the temperature of which had been previously adjusted to that desired. When the resistance in the cell became perfectly constant the measurement was taken. Subtracting from this resistance the resistance of the leads which had been previously measured on the same bridge, the actual resistance of the liquid in the cell was obtained. The cell was then emptied and the procedure repeated several times with fresh solution.

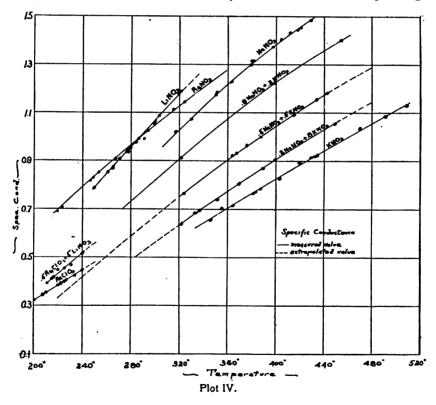
In order to determine what effect the level of the liquid in the cell might have on the cell constant different quantities of liquid were put into the cell and its resistance determined. From these measurements it was found that as long as the height of the liquid was a few millimeters above the upper angle of the elbow, it had no effect on the resistance. No change in the cell constant could be observed upon repeatedly taking the cell apart and reassembling it or upon heating it to a high temperature and then cooling it.

The procedure in determining the conductivity of the fused salts was similar to that followed in measuring the cell constant. The cell was assembled and sufficient salt introduced to fill the ends to the desired level when the salt was fused. The cell was then hung in position in the electric furnace previously described, the mica cover put in place and the thermo-electric couple adjusted so that the junction was immediately above and touching the tube B. The furnace was brought to any desired constant temperature and the resistance of the salt repeatedly measured until it became constant. Between each measurement the cell was tilted back and forth so as to introduce fresh liquid in the capillary. The corresponding temperature was then measured and from these data and the cell constant corrected for temperature, the specific conductance of the salt was calculated. The value of the cell constant k at the temperature of the fused salt was computed by means of the formula

32

$$k_1 = k_{18} \frac{1 + at}{(1 + \beta t)^2}$$

where  $\alpha$  = coefficient of expansion parallel to axis of cylinder and  $\beta$  = coefficient of expansion perpendicular to axis of cylinder. The expansion coefficients for quartz were taken from data by Randall<sup>1</sup> and a plot constructed with values of  $k_{i}$  as ordinates and corresponding



temperatures as abscissæ. From this plot the cell constant at any

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### No. 1.] CONDUCTANCE OF FUSED SALTS.

ferent temperatures. By plotting these data the resistance at any given temperature could be graphically interpolated.

*Results.*— The final results which we have obtained on the specific conductance  $\kappa$  of the fused salts investigated are given in the following tables. Tables X. to XIV. contain the mean results on

Temperature.	Specific Conductance «.	Temperature.	Specific Conductance «
318.7	1.022	404.3	1.402
329.7	1.073	411.4	1.433
349.8	1.172	417.9	1.448
351.1	1.184	420.1	1.456
363.3	1.228	428.9	1.487
378.5	1.299	446.3	1.570
379.7	1.316	459.9	1.595
381.6	1.318	477.6	1.697
397.8	1.376		

TABLE X.

TABLE Xa.

Temp.	Specific Conductance	Temp. Coef. 10 <sup>4</sup> C <sub>t</sub> .	Molecular Volume ø.	Equivalent Conductance $\Delta = \phi \kappa$ .	Temp. Coel 10 <sup>4</sup> C <sub>f</sub> '.
305 M.P.	0.9510		44.32	42.15	
310	0.9768	50.7	44.40	43.37	54.8
320	1.027	47.6	44.57	45.77	
330	1.077	43.6	44.74	48.18	51.3 47.3
340	1.125	43.6	44.90	50.52	47.3
350	1.173	38.5	45.07	52.87	42.6
360	1.219	34.7	45.26	55.17	42.2
370	1.262	33.5	45.43	57.55	33.5
380	1.305	30.2	45.60	59.51	33.7
390	1.345	28.6	45.77	61.56	32.4
400	1.384	27.1	45.95	63.59	30.8
410	1.422	25.0	46.12	65.58	28.9
420	1.458	24.4	46.29	67.50	28.2
430	1.494	22.2	46.47	69.43	26.2
440	1.528	22.0	46.65	71.28	20.4
450	1.562	21.0	46.83	73.15	23.9
460	1.595	21.0	47.01	74.98	24.7
470	1.628	18.0	47.19	76.83	24.0
480	1.658	18.0	47.38	78.56	22.0
490	1.687	16.0	47.56	80.23	
500	1.716	10.0	47.75	81.94	21.0

Specific and Equivalent Conductance of NaNO<sub>3</sub>.

the pure salts, and Tables XV. to XVIII. those on the mixtures. These data have been plotted, as shown on a reduced scale in plot IV., values of the specific conductance being taken as ordinates and corresponding temperatures as abscissæ. From the curves best representing these data the values of the specific conductance for

|--|

Temperature.	Specific Conductance Observed, x.	Temperature.	Specific Conductance Observed, s.
346.1	0.6563	429.0	0.9179
355.3	0.7047	432.0	0.9204
364.5	0.7179	434.2	0.9250
381.1	0.7662	474.4	1.039
382.5	0.7710	491.0	1.086
387.5	0.7887	508.9	1.131
403.4	0.8291		
420.0	0.9000		

Specific Con	ductance d	of .	Κľ	VO,	•
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TABLE XIa.

Temperature.	Specific Conductance,	<b>Temp. Coef.</b> 10 <sup>4</sup> C <sub>i</sub> .	Molecular Volume, ¢.	Equivalent Conductance $\Lambda = \phi \kappa$ .	Temp. Coef. 10 <sup>4</sup> C <sub>t</sub> '.
333.7 M.P.	0.6225	49.0	53.96	33.59	53.5
340	0.6420	46.8	54.11	34.74	50.6
350	0.6728	44.6	54.31	36.54	48.3
360	0.7035	43.1	54.51	38.35	47.3
370	0.7345	40.7	54.75	40.21	44.6
380	0.7650	40.7 39.1	54.96	42.04	43.5
390	0.7955		55.20	43.91	
400	0.8255	37.1	55.41	45.74	40.8
410	0.8558	36.1	55.66	47.63	40.4
420	0.8858	34.5	55.87	49.49	38.3
430	0.9153	32.8	56.08	51.33	36.6
440	0.9445	30.4	56.34	53.21	35.9
450	0.9730	29.7	56.56	55.03	33.6
4 <i>6</i> 0	1.001	27.5	56.78	56.83	32.2
470	1.029	27.6	57.02	58.67	31.9
480	1.056	25.9	57.24	60.45	28.9
490	1.083	25.2	57.49	62.26	<b>29.4</b>
500	1.109	23.8	57.75	64.04	_ 28.2
510	1.135	23.2	57.98	65.81	27.3

Specific and Equivalent Conductance of KNOs.

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310

1.126

each salt and mixture have been interpolated for ten-degree intervals. These values are given in Tables Xa to XVIIIa and form the basis of our later discussion.

## TABLE XII.

Specific Conductance of LiNOs.

Temperature.	Specific Conductance Observed, «.	Temperature.	Specific Conductance Observed, «.
244.9	0.0813	279.7	0.9513
248.5	0.7806	284.3	0.9706
261.4	0.8540	290.6	0.9897
264.9	0.8669	299.0	1.057
265.2	0.8758	299.3	1.068
270.2	0.9103	303.7	1.093
275.9	0.9374	319.4	1.182
276.2	0.9384	321.5	1.188
276.9	0.9381		
277.8	0.9327		

TABLE XIIa.

Temperature.	Specific Conductance, K.	Temp. Coef. 10 <sup>4</sup> C.	Molecular Volume, ¢.	Equivalent Conductance $\Lambda = \phi \kappa$ .	Temp. Coef. 10 <sup>4</sup> C <sub>4</sub> '.
250 M.P. 260	0.8448	68.8 63.4	38.50 38.63	30.36 32.63	72.1 67.0
270 280 290	0.9001 0.9570 1.013	61.3 56.8	38.76 38.89 39.00	34.89 37.22 39.51	64.6 59.7
300	1.069	53.7	39.13	41.83	57.0

Specific and Equivalent Conductance of LiNO<sub>3</sub>.

TABLE XIII.

39.27

51.9

Specific Conductance of AgNO3.

Temperature.	Specific Conductance Observed, κ.	Temperature.	Specific Conductance Observed, <i>x</i> .
200.0	0.0102	267.0	0.9083
21 <b>9.7</b>	0.6885	286.1	0.9921
223.5	0.7056	294.1	1.025
246.6	0.8172	315.0	1.113
248.9	0.8286	324.0	1.143
253.6	0.8516		
254.0	0.8523		

35

56.7

44.21

Confining our attention first, to the results on pure salts we have in Tables X*a* to XIV*a* in addition to the values of the specific conductance, column two, the values of the temperature coefficient  $C_t \times 10^4$  at  $t = 1/2(t_1 + t_2)$ , column three. This was computed for each tendegree interval on the assumption that over this range of temperature the variation of conductance is linear, *i. e.*,

36

$$C_t = \frac{\mathbf{I}}{\mathbf{I}/2(\kappa_1 + \kappa_2)} \cdot \frac{\kappa_2 - \kappa_1}{t_2 - t_1}$$

Inspection of the plot shows this to be very approximately the case. In column four are given values of the equivalent volume  $\phi$  at the

Temp.	Specific Conductance, <sup>K</sup> .	Temp. Coef. 10 <sup>4</sup> C <sub>t</sub> .	Molecular Volume, ¢.	Equivalent Conductance $\Delta = \phi \kappa$ .	Temp. Coef $10^4 C_t'$ .
218 M.P.	0.6815	69.6	42.88	29.22	71.5
230	0.7400	61.5	43.01	31.83	
240	0.7870	57.9	43.14	33.95	60.8
250	0.8340	53.7	43.26	36.08	59.1
260	0.8800	48.8	43.38	38.28	49.0
270	0.9240	45.0	43.50	40.20	47.8
280	0.9665	42.1	43.63	42.17	43.8
290	1.008	40.2	43.75	44.10	45.7
300	1.049	37.4	43.89	46.16	37.5
310	1.089	35.2	44.00	47.92	38.2
<b>320</b>	1.128	33.1	44.14	49.79	35.9
330	1.166	32.1	44.26	51.61	36.3
340 350	1.204 1.245	32.4	44.39 44.52	53.45 55.43	36.4

TABLE	XIIIa.
Specific and Equivalent	Conductance of AgNO <sub>2</sub> .

TABLE XIV.

Temperature.	Specific Conductance Observed, «.	Temperature.	Specific Conductance Observed, «
197.0	0.0256	222.2	0.3903
200.5	0.3210	225.1	0.3978
207.3	0.3468	226.4	0.4030
210.1	0.3531	234.0	0.4232
220.8	0.3853	240.0	0.4444

Specific Conductance of AgClO<sub>3</sub>.

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## TABLE XIVa.

Temperature.	Specific Conductance, <sup><i>K</i>.</sup>	Temp. Coef. 10 C <sub>t</sub> .	Molecular Volume, ¢.	Equivalent Conductance, $\Lambda = \phi \kappa$ .	Temp. Coef. 104 <i>Ci</i> '.
200	0.3219	91.3	48.65	15.66	101.0
210	0.3527	91.3 82.7	49.11	17.32	87.0
215	0.3676	82.7 81.6	49.22	18.09	86.6
220	0.3829	76.6	49.33	18.89	80.8
230	0.4134	70.0	49.55	20.48	77.0
240	0.4444	65.2	49.78	22.12	69.8
250	0.4743	UJ.4	50.00	23.72	09.5

Specific and Equivalent Conductance of AgClO,.

corresponding temperatures (taken from Tables Ia to Va) and in column five the values of the equivalent conductance  $\Lambda = \phi \kappa$ . The last column contains values of the temperature coefficient of the equivalent conductance  $C'_t$  at  $t = 1/2(t_1 + t_2)$  degrees, computed for each ten-degree interval by the formula

 $C_t' = \frac{1}{1/2(\Lambda_1 + \Lambda_2)} \cdot \frac{\Lambda_2 - \Lambda_1}{t_2 - t_1}.$ 

The above results on the specific conductance of sodium and potassium nitrates are in good agreement with those recently obtained by Kalmus<sup>1</sup> in Professor Lorenz's laboratory at Zürich. Thus the average difference between his values and ours for sodium nitrate is only a few tenths per cent., an agreement eminently satisfactory in view of the entire independence of the methods and form of apparatus used. In fact, our measurements and those of Kalmus appear to be the only ones among all previously published results which do agree well, those of Poincaré and of Foussereau on these same salts being 8 to 10 per cent. higher. We regard this agreement as lending great weight to the results of both these investigations and to the reliability of the methods employed. As sodium and potassium nitrates are the only two salts common to our investigation and that of Kalmus, a comparison of other values is impossible.

From a study of Tables Xa to XIVa and of the curves representing the corresponding data, the following conclusions may be drawn :

<sup>1</sup>Zeit. für Phys. Chem., 59, pp. 17, 244, 1907.

First : The specific conductance of fused sodium, potassium, and silver nitrates is not a linear function of the temperature but increases less and less rapidly as the temperature rises. Thus the change per degree in the specific conductance of sodium nitrate decreases from 0.0050 at  $310^{\circ}$  to 0.0036 at  $410^{\circ}$ ; for silver nitrate the change decreases from 0.0047 at  $230^{\circ}$  to 0.0038 at  $330^{\circ}$ .

Second : The specific conductance of lithium nitrate and of silver chlorate is, within the error of experiment, and over the smaller temperature range (about  $50^{\circ}$ ), which their limited stability permitted them to be investigated, a linear function of the temperature. The precision of the results on these salts is not as great as in the case of the other nitrates. Lithium nitrate, owing to its great hygroscopic tendency, was particularly difficult to investigate.

Third: The equivalent conductance of all salts investigated increases with the temperature, the percentage increase per degree being greater in every case than the corresponding percentage change of the specific conductance at the same temperature.

Fourth : The rate of increase of both specific and equivalent conductance becomes less the higher the temperature, but the decrease in rate is less marked in the case of equivalent than in the case of specific conductance.

Fifth: The temperature coefficient of a salt in the fused state is much less than the temperature coefficient of its aqueous solution.

We next investigated the conductance of mixtures of two salts possessing a common ion, namely NaNO<sub>3</sub> and KNO<sub>3</sub>. Previous experiments made by one of us<sup>1</sup> on the electromotive force of certain voltaic cells containing fused mixtures as electrolytes, indicated that the law of mass action holds in these mixtures as well as in aqueous solutions and that the dissociation of each salt is therefore affected, — depressed, — by the presence of the other. If this be the case then the conductance of the resulting mixture

\_\_\_\_

the corresponding density (see Tables VI. to VIII.); in column four the corresponding equivalent conductance, i. e.

$$\Lambda = \frac{\kappa}{D} \frac{(n_1 M_1 + n_2 M_2)}{n_1 + n_2},$$

where  $n_1$  and  $n_2$  are the number of mols of the two salts of molecular weights  $M_1$  and  $M_2$  respectively, in the mixture.

In the fifth column is given the value of the equivalent con-

 TABLE XV.

 Specific Conductance of 2 Mols KNO<sub>3</sub> + 8 Mols NaNO<sub>3</sub>.

	•	• •	•
Temperature.		Specific C	Conductance served.
		06	served.

Temperature.	Observed.
321.6	0.9119
399.1	1.224
454.1	1.401

TABLE XVa.

Specific Equivalent Conductance of 2 Mols KNO<sub>3</sub> + 8 Mols NaNO<sub>3</sub>.

Temperature.	Specific Con- ductance, «.	• Density, D.	Equivalent Conductance.	Equivalent Conductance Computed.	Difference
274	0.7025	1.937	32.03		
290	0.7735	1.925	35.48		
300	0.8185	1.918	37.69		
310	0.8623	1.910	39.87		
320	0.9048	1.903	41.99	l .	
330	0.9480	1.896	44.15		
340	0.9905	1.888	46.33	47.36	-1.03
350	1.032	1.881	48.45	49.60	-1.15
360	1.073	1.874	50.56	51.81	-1.25
370	1.110	1.866	52.53	54.09	-1.56
380	1.153	1.859	54.77	56.02	-1.35
390	1.191	1.852	56.79	58.03	-1.24
400	1.227	1.844	58.76	60.02	-1.26
410	1.262	1.837	60.67	61.99	-1.32
420	1.295	1.830	62.49	63.90	-1.41
430	1.327	1.823	64.28	65.81	-1.53
440	1.358	1.815	66.07	67.67	-1.60
450	1.389	1.808	67.84	69.33	-1.69

ductance of the mixture computed from the conductance of the components, i. e.,

$$\Lambda = \frac{n_1 \Lambda_1 + n_2 \Lambda_2}{n_1 + n_2}$$

and in the last column the difference between the observed and computed values.

It is evident from a study of these differences that the equivalent conductance of mixtures of sodium and potassium nitrate is less than that computed from the conductance of the components of the mix-

Table XVI.	TA	BLE	X	VI	
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#### Specific Conductance of 5 Mols KNO<sub>8</sub> + 5 Mols NaNO<sub>8</sub>.

Temperature.	Specific Conductance Observed, «.	Temperature.	Specific Conductance Observed, s.
323.9	0.7625	387.6	0.9981
364.2	0.9262	414.7	1.091
367.4	0.9313	433.5	1.155
376.2	0.9645	442.0	1.181

# TABLE XVIa.

Temp.	Specific Conductance, «.	Density, D.	Equivalent Conductance.	Equivalent Conductance Computed.	Difference.
220	0:3300	1.967	13.64		
300	0.6630	1.907	32.23		
310	0.7043	1.899	34.54		
320	0.7475	1.892	36.80		
330	0.7890	1.884	39.01		
340	0.8293	1.876	41.17	42.63	-1.46
350	0.8680	1.869	43.25	44.71	-1.46
360	0.9050	1.862	45.27	46.76	-1.49
370	0.9410	1.854	47.27	48.88	-1.61
380	0.9768	1.847	49.26	50.78	-1.52
390	1.011	1.839	51.20	52.74	1.54
400	1.045	1.832	53.13	54.67	-1.54
410	1.078	1.824	55.05	56.61	-1.56
420	1.111	1.817	56.95	58.50	-1.65
430	1.143	1.809	58.85	60.38	-1.53

Equivalent Conductance of 5 Mols KNO<sub>2</sub>+ 5 Mols NaNO<sub>3</sub>.

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## TABLE XVII.

Temperature.	Specific Conductance Observed.	Temperature.	Specific Conductance Observed.
322.4	0.6392	369.4	0.8055
332.7	0.6849	388.7	0.8684
337.1	0.6930	398.5	0.9004
352.4	0.7399	449.0	1.055

Specific Conductance of 8 Mols KNO<sub>3</sub> + 2 Mols NaNO<sub>3</sub>.

### TABLE XVIIa.

Temp,	Specific Conductance, «.	Density, D.	Equivalent Conductance.	Equivalent Conductance Computed.	Difference
284 M.P.	0.5013	1.914	25.66		
300	0.5600	1.902	28.84		
310	0.5955	1.896	30.77		
320	0.6318	1.889	32.77		
330	0.6668	1.881	34.73		
340	0.7015	1.873	36.69	37.90	-1.21
350	0.7358	1.866	38.63	39.81	-1.18
360	0.7705	1.858	40.62	41.71	-1.01
370	0.8055	1.851	42.63	43.68	-1.05
380	0.8393	1.843	44.61	45.53	-0.92
390	0.8730	1.835	46.62	47.44	-0.82
400	0.9053	1.828	48.52	49.31	-0.79
410	0.9370	1.820	50.44	51.22	-0.78
420	0.9678	1.812	52.35	53.09	-0.74
430	0.9983	1.805	54.18	54.95	0.77
440	1.028	1.797	56.04	56.82	0.78
450	1.059	1.790	57.96	58.65	-0.69

Equivalent Conductance of 8 Mols KNO<sub>2</sub> + 2 Mols NaNO<sub>2</sub>.

ture. The mutual effect of the two salts on each other is to decrease the conductance of one or both of the salts by an amount dependent upon the composition of the mixture. The difference between observed and calculated values is as great as 4 per cent., being a maximum for the equimolecular mixture. This difference, though small, cannot be accounted for on the ground of experimental error. The effect of mixing these two salts must be therefore to change either their degree of ionization or the migration velocity of their ions, or both. We have independent evidence for believing that their dissociation is somewhat diminished; we shall see later from the measurements of the viscosity of the same mixtures that in them the ionic velocities may be greater than in the pure salts.

The only other experiments thus far carried out which bear upon this problem are those by Bouty and Poincaré<sup>1</sup> and by Poincaré.<sup>2</sup>

They also investigated the conductance of mixtures of sodium and potassium nitrate and came to the conclusion that the conductance of the mixture was equal to the conductance computed from that of the components. Since however the agreement found by them was only within about I to 4 per cent., the above effect shown by our experiments would not have been evident.

We also investigated the conductance of a mixture consisting of two dissimilar salts possessing no common ion, namely, lithium

Temperature.	Specific Conductance Observed, <i>x</i> .	Temperature.	Specific Conductance Observed, «.
211.5	0.3949	225.0	0.4447
214.5	0.4111	231.0	0.4637
216.0	0.4169	240.0	0.5132
220.0	0.4503	240.7	0.5137
220.0	0.4506 ·		

TABLE XVIII.

Specific Conductance of 5 Mols LiNO<sub>2</sub> + 5 Mols AgClO<sub>3</sub>.

TABLE XVIIIa.

Temperature.	Specific Conductance, «.	Density, D.	Equivalent Conductance.	Equivalent Conductance Computed.	Difference
210	0.3890	2.968	17.07	19.57	-2.50
220	0.4306	2.957	18.96	21.43	-2.47
230	0.4719	2.946	20.86	23.32	-2.46
240	0.5132	2.936	22.76	25.23	-2.47
250	0.5553	2.925	24.72	27.12	-2.40

Equivalent Conductance of 5 Mols LiNO<sub>8</sub> + 5 Mols AgClO<sub>8</sub>.

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No. 1. ] FLUIDITY OF FUSED SALTS.

nitrate and silver chlorate. Here a metathesis is possible between the salts according to the reaction

$$LiNO_{3} + AgClO_{3} = AgNO_{3} + LiClO_{3}$$
.

If the degree of ionization of the products of this reaction is materially less than that of the initial salts, the resulting conductance will be less than the sum of conductances of the components. Inspection of columns four and five in Table XVIII*a* shows this to be the case; the observed equivalent conductance is more than 10 per cent. less than that computed from the component salts, indicating the formation of considerable undissociated salt. It is to be noted that our experiments on the density of this mixture, see Table IX., indicated a marked contraction of volume (16 per cent.) upon mixing the components. These experiments further emphasize the influence of the presence of one salt on the ionization of another. Unfortunately the effect in the above case cannot yet be computed for lack of data on the absolute dissociation of the salts concerned.

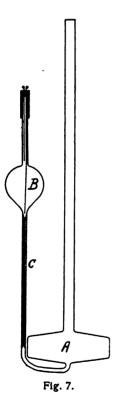
# IV. VISCOSITY - FLUIDITY - MEASUREMENTS.

The third part of our investigation was devoted to the determination of the viscosity of the fused salts previously investigated. The only previous work done on this class of substances was that of Foussereau<sup>1</sup> who in 1885 determined the viscosity of fused sodium and potassium nitrates and of their mixtures by Pousseuille's capillary tube method. The results obtained lead him to conclude that viscosity and specific conductance varied reciprocally or otherwise expressed, that the fluidity of a fused salt and its specific conductance were directly proportional. As our results on the specific conductance of sodium and potassium nitrate failed entirely to confirm those of Foussereau the above conclusion drawn by him seemed also open to question. We therefore attempted to determine the viscosity of the salts we had previously investigated with a precision of one

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We first attempted to construct our viscosity apparatus of glass, but found that with all samples of glass capillaries available, an etching occurred which not only rendered the constant of the apparatus uncertain, but also tended to contaminate the electrolyte. Unfortunately fused guartz capillaries were not obtainable without long delay so that we finally devised an apparatus of platinum which gave very satisfactory results.

The apparatus is shown in Fig. 7. It will be seen to be a



modification of the well known form of apparatus used for relative viscosity measurements. The capillary C was 0.6 mm. diameter and 100 mm. long, and enclosed in a tube of platinum 3 mm. diameter to protect it from injury.

The volume of the bulb B was 10 c.c. and that of the lower reservoir A 100 c.c. approxi-The form of each of these reservoirs mately. is shown in the figure;  $A_{i}$  was approximately cylindrical in form and of large cross-section. To reduce expense, this portion of our apparatus was constructed of silver instead of platinum by which the range of temperature over which it could be used was limited. If constructed wholly of platinum the apparatus may be used up to any temperature at which the salts investigated remain undecomposed.

The salt was first introduced as powder and melted in the reservoir A. It was then forced up by means of compressed air through the capillary C until the bulb B was completely filled and allowed to flow back into A under

the influence of gravity. The novel feature of the apparatus was the method of noting the time it took the liquid in the bulb B to flow back through the capillary. This was accomplished by noting

## No. I.] FLUIDITY OF FUSED SALTS. 45

lower end of the bulb B where it joins the capillary. The time of breaking these circuits was noted by means of a telephone placed in series with an induction coil. When the two electrodes were properly centered, the time of flow could be determined with a precision of about one second in 800 seconds. The whole apparatus was immersed in the fused nitrate bath described in Section I., thus enabling a very uniform temperature to be maintained throughout.

Corrections. — The coefficient of viscosity of a liquid flowing through a capillary tube is given by the well-known formula<sup>1</sup>

$$\eta = \frac{\pi r^A p t}{8 v l} - \frac{d v}{8 \pi l t},$$

in which the second term is a small correction for the kinetic energy of the liquid issuing from the capillary. In this formula l is the length and r the radius of the capillary, and t the time it takes a volume v of the liquid of density d to flow through the capillary under a pressure p.

For a given capillary this expression may be written

$$\eta = pt \left[ A_1 - \frac{B_1}{t^2} \right],$$

• where  $A_1$  and  $B_1$  are constants.

The constant  $A_1$  is independent of the temperature since its effect on the change in cross-section of the capillary is just offset by the change in volume of liquid flowing through the capillary and in its length. The effect of temperature on the value of  $B_1$  may be neglected as this constant enters only in a small correction term.

The pressure p is proportional to the density of the liquid and the height through which the liquid falls. The density is known for each liquid over the range of temperature investigated. The height varies with the temperature as the first power of the linear material composing the capillary. The expression for the viscosity may therefore be written

$$\eta = dt(1 + a\theta) \left[ A + \frac{B}{t^2} \right]$$

where A and B are constants independent of  $\theta$ . These constants may be determined by calibrating the apparatus with a liquid (water) of known viscosity at two different temperatures. The viscosity of any other liquid may then be determined by measuring its time of flow t through the same apparatus at a known temperature  $\theta$ .

One other correction was applied to eliminate the effect of change in head of the liquid on the time of flow, due to change in cross-section of the reservoir A and expansion of the liquid. This correction was very small, never exceeding a few tenths of one per cent. It was determined as follows:

The apparatus was calibrated with water at 0° C. and  $\theta$ ° C. Suppose the corresponding volumes of liquid in the reservoir A to be  $v_0$  and  $v_0$ . At  $\theta$ ° the cross-section of the reservoir increased from  $s_0$  to  $s_0(1 + 2\alpha t)$ . In order therefore that the liquid should stand at the same level as at 0° its volume should be  $v_0(1 + 2\alpha t)$ . It is, however,  $v_0$  and therefore the quantity

$$\frac{v_0(1+2at)-v_0}{1+2at} = v_0 - \frac{vt}{1+2at}$$

represents the resulting change in height of the liquid in the reservoir A, assumed cylindrical. If therefore x represents the change in the time of flow through the capillary with change of head we have

t corrected = t observed 
$$\left[ 1 + \left( v_0 - \frac{v_t}{1 + 2at} \right) x \right]$$
.

The value of x was determined experimentally and found to be 0.00233. In the case of the fused salts the values of the volume were computed from the data on the density and known weight of salt used.

The following values of the absolute viscosity of water were used in computing the values of the constants A and B. These are the best average values taken from the investigations of Gartenmuster,



### FLUIDITY OF FUSED SALTS.

No. I.]

Heydweiller, Noack, Pacher, Pousseuille, Slotte, Sprung, Thorpe and Rodger, Grotrian, Meyer and Wagner. All values given later for

l'emperature.	<b>ΙΟ<sup>6</sup>η</b>	Temperature.	<b>ΙΟ<sup>6</sup>η</b>
. 0	1797	19	1029
5	1518	20	1004
10	1307	21	980
15	1140	22	957
16	1110	23	936
17	1082	24	915
18	1055	25	895

Values of Viscosity of Water.

the viscosity and fluidity are therefore absolute, not relative values, and are based on the above values for water as standards.

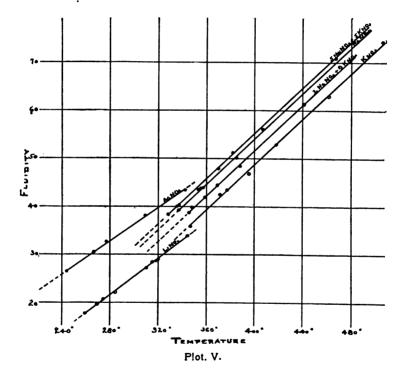
It should be stated that the constants of our apparatus varied from time to time in an irregular and unexplained manner by one per cent. or more in much the same way as described by Bousfield<sup>1</sup> in his researches. We therefore made it a point to determine its constants with water *immediately before and after every series of measurements*. If the constants were found to have changed by over 0.75 per cent. the measurement was discarded. The agreement was usually much better than this, in which case the mean values of the constants before and after the run were taken in the computation.

A test of our apparatus and of the value of its constants was made on a one per cent. solution of sodium chloride. Two determinations at  $22.8^{\circ}$  C. gave for its viscosity 0.00962 and 0.00958respectively as compared with Hosking's value 0.00959. The agreement is entirely satisfactory.

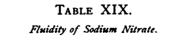
*Results.* — In presenting the results of our work on viscosity we have found it more convenient to consider the reciprocal of the viscosity or fluidity, as this quantity varies directly instead of reciprocally with the temperature. We have therefore computed the value of  $F = 1/\eta$  for each of the salts and salt mixtures and the results are tabulated in Tables XIX. to XXIV. and shown graphically on a reduced scale in Plot V. where the fluidities are plotted as ordinates and temperatures as abscissæ. It will be seen that the best repre-

<sup>1</sup> W. R. Bousfield, Zeit. fur phys. Chem., 53, 257, 1905.

sentative curves are in all cases straight lines; that is, within the limits of experimental error (about 1 per cent.), the fluidity of fused sodium, potassium, lithium and silver nitrate is directly proportional to the temperature. Silver chlorate was not investigated on account of the danger of an explosion in the nitrate bath.



In Tables XIXa to XXIVa are given the values of the fluidity interpolated from the original plots, at intervals of ten degrees. In



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FLUIDITY OF FUSED SALTS.

column three is given the value of the corresponding temperature coefficient multiplied by  $10^4$  for each interval, *i. e.*,

$$C_{i} = \frac{1}{\frac{1}{2}(F_{1} + F_{2})} \cdot \frac{F_{2} - F_{1}}{t_{2} - t_{1}}$$

at  $t = \frac{1}{2}(t_1 + t_2)$ .

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Column four contains the value of the ratio of the specific conductance to the fluidity multiplied by  $10^4$ , *i. e.*,  $10^4 \kappa/F$ .

In the fifth column we have computed the values of the fluidity F divided by the corresponding molecular volume  $\phi$  of the liquid; this we have denoted by f and called the molal fluidity. This

Temperature.	F Interpolated from Plot.	Temperature Coefficient, 10 <sup>4</sup> C <sub>1</sub> .	104 <mark>#</mark> F		Temperature Coefficient 10 <sup>4</sup> C <sub>t</sub> '.	Å 7
340	40.4	53	278	0.900	49	56.0
350	42.6	53	275	0.945	42	55.9
360	44.9	- 50 - 50	272	0.985	44	56.1
370	47.2	48	268	1.03	48	55.9
380	49.5	45	264	1.08	46	55.2
390	51.8	42	260	1.13	44	54.5
400	54.0	42	256	1.18	42	54.0
410	56.4	40	253	1.23	40	53.4
420	58.7	39	250	1.28	38	53.0
<b>430</b> <sup>°</sup>	61.0	39	246	1.31	36	53.0
440	63.3	38	242	1.36	36	52.2
450	65.7	34	238	1.40	35	52.3
460	68.0	34	234	1.45		51.8
470	70.2	32	•			
480	72.5	32				
490	74.9	32 30				

Τ	ABLE	$\mathbf{XI}$	$\mathbf{X}a$ .
Т	ABLE	XI	Xa.

Fluidity of Sodium Nitrate

Т	AB	LE	х	Х.
-				

Fluidity of Potassium Nitrate.

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quantity is proportional to the number of mols of the fluid-which in unit time pass through the viscosity apparatus, since its reciprocal

$$\frac{1}{f} = \frac{\phi}{F} = \phi\eta$$

is the product of the molecular volume and viscosity or in other words a quantity proportional to the time required for one molecular weight of the liquid to pass through the capillary. For purposes of comparison with the equivalent or molecular conductance

Tempera- ture.	F Interpolated from Plot.	Tempera- ture Coeffi- cient $10^4 C_t$ .	104 <del>K</del>		Tempera- ture Coeffi- cient, $10^4 C_t'$ .	Å 7
340	36.1	51	178	0.666	47	52.3
350 360	38.0 40.1	54 53	1 <b>77</b> 1 <b>75</b>	0.698 0.736	53	52.3 52.2
370 380	42.3 44.5	51	174 172	0.775 0.810	52 42	51.7 52.2
390 400	46.7 48.8	48 44	170 169	0.845	41 37	51.9 51.9
410	51.1	- 43 42	167	0.923	38 31	51.6
420 430	53.3 55.6	41 40	166 165	0.959 0.989	33 29	51.6 51.9
440 450	57.9 60.2	39	163 162	1.022 1.062	34	51.9 51.9
460 470	62.5 64.8	38 37	160 159	1.100 1.139	35 35	51.6 51.6
480 490	67.1 69.4	36 35	157	1.174	31 28	51.7
490 500	71.8	34	156 155	1.207 1.243	29	51.5 51.4

TABLE	XX	2.
Fluidity of Pot	assium	Nitrate.

TABLE XXI.

Fluidity of Lithium Nitrate.

# TABLE XXIa.

Tempera- ture.	F Interpolated from Plot.	Tempera- ture Coeffi- cient, 10 <sup>4</sup> C <sub>f</sub> .	104 <del>K</del> F		Tempera- ture Coeffi- cient 10 <sup>4</sup> C <sub>f</sub> .	Å ₹
250 260 270 280 290 300 310 320 330 340 350	16.3 18.1 19.8 21.7 23.5 25.3 27.2 29.1 31.0 32.9 34.8	105 90 91 80 73 73 68 62 60 56	484 468 • 454 441 433 425 414	42.3 46.8 51.1 55.8 60.2 64.5 69.4	105 88 69 76 69 73	71.8 69.7 68.2 66.7 65.5 65.0 63.8

# Fluidity of Lithium Nitrate.

TABLE XXII.

Fluidity of Silver Nitrate.

Temperature.	Fluidity (F) Observed.	Temperature.	Fluidity (F) Observed.
244.0	26.5	309.0	38.3
265.5	30.5	342.0	43.5
275.0	32.8		

Fluidity of Silver Nitrate.

Temper- ature.	F Interpolated from Plot.	Tempera- ture Coeffi- cient, 10 <sup>4</sup> C <sub>i</sub> .	104 <mark>#</mark> F		Tempera- ture Coeffi- cient, Io <sup>4</sup> C <sub>i</sub> '.	<u>^</u> /
230	24.0	72	308	0.557	71	57.2
240	25.8	71	305	0.598	71	56.7
250	27.7	63	301	0.642	59	56.3
260	29.5	59	298	0.681	56	56.3
270	31.3	56	295	0.720	54	55.8
280	33.1	53	292	0.760	49	55.5
290	34.9	50	289	0.798	47	55.5
300	36.7	47	286	0.836	45	55.3
31Ó	38.5	43	_ 283	0.873	43	54.8
320	40.2	40	280	0.911	40	54.7
330	42.0	42	277	0.952	37	54.3
340	43.8	38	275	0.988	34	54.3
350	45.5		273	1.022		54.3

of the liquids, this function of the fluidity seems more rational to use than fluidity as ordinarily defined.

In column six is given the value of the temperature coefficient of f for each ten-degree interval and in column seven the ratio of the equivalent (molecular also in the case of the univalent salts here investigated) conductance to the molal fluidity.

## TABLE XXIII.

## Fluidity of 5 Mols KNO<sub>3</sub> + 5 Mols NaNO<sub>3</sub>.

Temperature.	Fluidity (F) Observed.	Temperature.	Fluidity (F) Observed.
328.0	38.5	370.0	47.8
335.0	40.0	382.0	51.3
337.3	40.2	468.0	70.5

## TABLE XXIIIa.

Temper- ature.	F Inter- polated from Plot.	Tempera- ture Coeffi- cient, 10 <sup>4</sup> C <sub>1</sub> .	104 <del>/</del>		Tempera- ture Coeffi- cient, 10 <sup>4</sup> C <sub>t</sub> '.	Å 7	Molal Fluidity, f' Com- puted.	S-S'
340	41.1	56	196	0.826	58	49.7	0.783	0.043
350	43.5	50	1 <b>99</b>	0.875	46	49.4	0.822	0.053
360	45.7	49	198	0.916	36	49.5	0.860	0.056
370	48.0	49 47	196	0.949	52	49.7	0 900	0.049
380	50.3	47	194	1.000	38	49.3	0.945	0.055
390	52.6	45	1 <b>92</b>	1.039	34	50.6	0.987	0.052
400	54.8	41	191	1.075	45	49.7	1.030	0.045
410	57.2	38	189	1.124	40	48.7	1.076	0.048
420	59.4	38	187	1.160	34	49.2	1.119	0.041
430	61.7	30	185	1.200	31	49.2	1.149	0.051
440	64.0	37	183	1.238	31	49.0	1.191	0.047
450	66.3	35	181	1.277	51	49.1	1.231	0.046

### Fluidity of 5 Mols KNO<sub>2</sub> + 5 Mols NaNO<sub>2</sub>.

## TABLE XXIV.

Fluidity of 8 Mols KNO<sub>3</sub> + 2 Mols NaNO<sub>3</sub>.

Temperature.	Fluidity (F) as Observed.	Temperature.	Fluidity (F) as Observed.
345.0	38.9	369.5	44.5
347.0	40.0	388.0	48.4
358.5	42.0	441.0	61.4

### TABLE XXIVa.

Tempera- ture.	Finterpo- lated from Plot.	Tempera- ture Coef- ficient, 10 <sup>4</sup> C <sub>t</sub> .	104 <b>#</b> F		Tempera- ture Coef- ficient, 10 <sup>4</sup> C <sub>t</sub> '.	Å ₹	Molal Fluidity, f' Com- puted.	5-J'
340	38.6	51	184	0.735	45	49.8	0.713	0.022
350	40.6	55	183	0.769	50	50.2	0.747	0.022
360	42.9	50	181	0.808	53	50.3	0.786	0.022
370	45.1	50	180	0.852	45	50.0	0.826	0.026
380	47.4	46	179	0.891	40	50.0	0.864	0.027
390	49.6	46	177	0.927	41	50.3	0.892	0.025
400	51.9	44	176	0.966	42	50.2	0.940	0.026
410	54.2	39	174	1.007	40	50.3	0.984	0.023
420	56.4	40	172	1.048	35	50.0	1.023	0.025
430	58.7	38	171	1.085	32	49.8	1.053	0.032
440	61.0	30	169	1.120	32	50.1	1.089	0.031
450	63.3	37	168	1.156	31	50.3	1.129	0.027
460	65.7	5/						

Fluidity of 8 Mols KNO<sub>3</sub> + 2 Mols NaNO<sub>3</sub>.

A consideration of the results on the pure salts contained in Tables XIXa to XXIIa leads to the following conclusions:

Comparing first the values of the temperature coefficients in column three with the values of the corresponding coefficients for specific conductance (see pp. 33-36) it will be seen that the rate of change of fluidity is greater than the change in conductance, *i. e.*, with increasing temperature the fluidity increases more rapidly than the specific conductance, and hence, as shown in column four, the ratio of  $\kappa/F$  decreases with increasing temperature. This is the case with all four salts investigated. The decrease in the ratio is very marked, being 9, 10 and 13 per cent. for potassium, silver and so-dium nitrates, respectively, for 100 degrees increase in temperature. For lithium nitrate the ratio decreases over 12 per cent. for an increase in temperature of only 50 degrees.

From this it follows that the specific conductance of fused salts is *not* strictly proportional to their fluidity.

The only existing data with which these results can be compared are those obtained by Foussereau in 1885 and Kalmus in 1907. Both of these investigators determined their viscosities by PousseuKalmus, but fail utterly to confirm those obtained by Foussereau. His measurements must, we believe, have been subject to some large sources of error.

That strict proportionality should obtain between the fluidity and specific conductance of fused salts seems to us *a priori* improbable. A more logical basis of comparison would seem to be between the corresponding molal properties of the salts in question. It was for this reason that we computed the values of the so-called molal fluidity,  $f = F/\phi$ , its temperature coefficient, and the ratio between it and the corresponding molecular conductance. The value of the molal fluidity f is itself a linear function of the temperature, since both F and  $\phi$  have been shown to vary directly with the temperature.

Comparing the values of its temperature coefficient given in column six with the corresponding values of the temperature coefficient of the equivalent conductance  $\Lambda$  (column six, Tables Xa to XIIIa) it will be seen that, while not identical, these agree very much closer in value than the coefficients compared above. This appears more evident from the values of the ratio

$$\frac{\Lambda}{f} = \frac{\text{molal conductance}}{\text{molal fluidity}}.$$

In the case of potassium nitrate the ratio may be regarded as constant when the magnitude of the experimental error resulting from the combined effect of errors in the viscosity, conductivity, density and temperature is considered. In fact, strict proportionality holds to within 2 per cent. over a range of  $150^{\circ}$ .

In the case of sodium nitrate the proportionality does not appear to hold quite as rigidly, the ratio decreasing 6 per cent. per  $100^{\circ}$  rise in temperature (350° to 450°). For the same temperature interval the ratio  $\kappa/F$  decreased 13 per cent.

No. 1.]

It would appear therefore that increasing the temperature increases the molecular conducting power of the fused salts studied in very nearly the same ratio as the molal fluidity. The latter appears to increase sli<sub>b</sub> htly more rapidly however, this being most marked in the case of sodium and lithium nitrate. The significance of this on dissociation will be pointed out below.

It should also be noted that the value of the ratio  $\Lambda/f$  is nearly the same for sodium, potassium and silver nitrates and their mixtures, *i. e.*,  $\Lambda/f$  = a constant for a group of similar salts.

Tables XXIII to XXIVa contain the results obtained on two nitrate mixtures. The relations obtaining in the case of the pure salts are very strikingly evident here. The ratio of the specific conductance to the fluidity decreases in both cases, namely, by g per cent. per 100° for the equimolecular mixture and by 8 per cent. per 100° for the 8 mols KNO, + 2 mols NaNO, mixture. On the other hand the ratio of the equivalent conductance to the molal fluidity  $\Lambda/f$  is practically constant over the entire range of temperatures investigated. The constancy of the ratio in these cases is in fact so marked that taken in conjunction with the results on the pure salts one is tempted to conclude that the relation in question is one which holds approximately true for fused salts in general. It is very desirable that this conclusion be further tested with additional data on salts of different types. We are unable at present to test this relation on the results obtained by Kalmus on lead chloride, lead bromide, and potassium bichromate as data on the molecular volume of these salts are still wanting.

One other interesting result is shown in the last two columns of Tables XXIIIa and XXIVa. From the molal fluidity of the components of the mixture the molal fluidity was computed by the mixture formula. These values are given in column eight, and in the last column, are given the differences between the observed and computed values. The observed fluidities are in all cases uniformly greater than the computed values. In the case of the equimolecular mixture the difference is about 5 per cent., the mixture having a fluidity uniformly greater than that of the component of greater fluidity. In the cases of the 8:2 mixture the difference is less but uniform in magnitude. It appears therefore, that, in the

cases investigated, the state of aggregation is so changed as a result of the solution of one salt in the other that the fluidity of the mixture is increased.

This is particularly interesting in view of the results previously obtained on the conductivity of the same mixtures. It was found, see p. 41, that the observed equivalent conductance of the mixtures was less than the computed value. Hence, if we assume as a first approximation, that the velocity of migration of ions in a given electrolyte is proportional to the fluidity of the medium through which they move, we have here additional evidence<sup>1</sup> that the dissociation of two salts possessing a common ion is diminished as required by the law of mass action when they are mixed.

If we assume that conduction in fused salts takes place in a similar manner to conduction in solutions then

$$\Lambda_{t} = \gamma_{t}(u+v)_{t}$$

where  $\gamma$  is the ionization constant of the salt and u and v are the ionic conductances. Both  $\gamma$  and (u + v) are functions of the temperature. If we further assume that the ionic velocities in fused salts are proportional to the molal fluidity of the medium through which the ions move (which reflection will show is more likely to be true the higher the degree of dissociation), *i. e.*, if we may put

$$(u + v)_i = kf_i$$
 where  $k = \text{constant}$ ,

then

$$\left(\frac{\Lambda}{f}\right)_{t} = k\gamma_{t}$$

From this it would follow that a comparison of the ratio of A/f at two different temperatures would give an indication of the change of dissociation of the salt between these temperatures. From such a comparison it appears that an increase in the temperature of 100° or more has only a slight effect on the ionization of the fused salts investigated, its tendency being to diminish rather than increase the dissociation. The decrease in dissociation is very small or zero in the case of potassium nitrate and its mixtures with sodium nitrate ; for silver nitrate it is 4.2 per cent. per 100°; for sodium nitrate 6.4 per cent. per 100°; for lithium nitrate 11 per cent. for 60°.

<sup>1</sup>Goodwin, PHYS. REV., 24, p. 77, 1907.



#### FLUIDITY OF FUSED SALTS.

No. 1.]

This result is not astonishing ; the recent accurate determinations of Noyes<sup>1</sup> on the ionization of *highly* dissociated salts at high temperatures in aqueous solution show that increasing the temperature produces a very marked diminution in the dissociation of the dissolved salt. The ionization of *slightly* dissociated substances like water, on the other hand, increases rapidly with increasing temperature. Our results lend decided weight therefore to the hypothesis of a high degree of dissociation in fused salts as maintained by Lorenz. Furthermore, the enormous increase in the conductivity of a salt at its melting point as it passes from the solid to the liquid state (an isothermal phenomenon) clearly points to some other factor than temperature as the cause to which its increase in value is to be chiefly ascribed.

If the assumptions upon which the above conclusion is based prove to be valid we may further conclude that the above nitrates ionize in the fused state with evolution of heat.

## SUMMARY.

The results of our investigation may be summarized as follows:

I. The density of fused sodium, potassium, lithium and silver nitrate and silver chlorate together with mixtures of sodium and potassium nitrate and of lithium nitrate and silver chlorate had been determined to 0.1 per cent. over a wide range of temperature.

In all cases the density was found to be a linear function of the temperature to within a tenth of a per cent. Tables giving the specific and molecular volume of the above salts for every ten degrees have been computed.

2. The specific volume of mixtures of sodium and potassium nitrate containing 8 and 2, 5 and 5, and 2 and 8 mols of these salts respectively is greater than that computed from the specific volumes of the components, *i. e.*, the solution of one salt in another is accompanied by an expansion. The magnitude of this expansion is small being a maximum, 0.5 per cent., for equimolecular mixtures.

In the case of an equimolecular mixture of lithium nitrate and silver chlorate on the other hand a contraction of 20 per cent. occurs.

<sup>1</sup>See Carnegie Institution Publications.

3. The specific conductance of the same salts and salt mixtures has been determined over the same temperature interval as the density. The results show that, except in the case of lithium nitrate and silver chlorate which could be measured over only a limited range of temperature on account of their instability, the specific conductance is not strictly proportional to the temperature but increases less and less rapidly as the temperature rises. For the limited range of temperature over which lithium nitrate, silver chlorate and their mixtures were studied, the specific conductance is proportional to the temperature. Tables have been computed giving the specific and equivalent conductance of each salt and mixture for every ten degrees as well as the temperature coefficient for each interval. The temperature coefficient is, generally speaking, less than one fifth as great as that for the corresponding aqueous solutions.

4. A study of the computed values of the equivalent conductance shows that this quantity increases very nearly linearly with the temperature. The temperature coefficient decreases therefore with increasing temperature but at any given temperature is slightly greater than that of the specific conductance at the same temperature.

5. The equivalent conductance of the mixtures of the sodium and potassium nitrate is less than that computed from the equivalent conductance of the components. This is most marked in the case of the equimolecular mixture where the difference reaches three per cent., an amount considerably greater than can be accounted for by experimental error. It tends to confirm the view that the effect of dissolving one nitrate in another is to decrease the dissociation. Our results do not confirm the conclusion drawn by Poincaré from similar experiments on the conductivity of mixed nitrates, namely, that the conductance of a mixture can be accurately calculated from that of the components by the mixture formula.

6. In the case of an equimolecular mixture of lithium nitrate and silver chlorate the deviations between observed and computed values of the equivalent conductance are as much as 12 per cent., the computed values being as before the larger, indicating a metathesis between the components with corresponding change (decrease) of ionization. This mixture also showed a contraction in volume of 16 per cent.



#### No. 1.]

7. The fluidity or reciprocal of the absolute viscosity coefficient of the same series of fused salts was measured over the temperature interval in which their conductivity and density were studied.

In all cases the fluidity was found to be directly proportional to the temperature. Its temperature coefficient is in every case greater than the corresponding temperature coefficient of specific conductance.

8. The ratio

$$\frac{\text{specific conductance}}{\text{fluidity}} = \frac{\kappa}{F}$$

contructed for every ten degrees, was found to decrease regularly without exception with increasing temperature. Foussereau's law of the proportionality between these quantities is therefore not confirmed. Our results are however in excellent agreement, so far as comparison is possible, with those of Lorenz and Kalmus.

9. The value of

$$f = \frac{\text{fluidity}}{\text{molecular volume}} = \frac{F}{\phi},$$

which we have called molal fluidity, and its temperature coefficient for each ten degrees was also computed. The results show that the molal fluidity is directly proportional to the temperature. The ratio

$$\frac{\text{molal conductance}}{\text{molal fluidity}} = \frac{\Lambda}{f}$$

has also been calculated for every ten degrees. This ratio is practically a constant for potassium nitrate and mixtures of potassium and sodium nitrate over a range of temperature of more than  $100^{\circ}$ . In the case of sodium, lithium and silver nitrates the proportionality does not hold quite as rigidly; the ratio decreases with increasing temperature by a few per cent., an amount however which we believe cannot be attributed wholly to experimental error. The ratio is approximately a constant for the group of nitrates investigated.



tion — analogous to its effect on salts in aqueous solutions raised to high temperatures under pressure as recently shown by Noyes. As this is characteristic of very highly dissociated substances our results lend weight to the view that a high rather than a low degree of ionization obtains in fused electrolytes.

10. The molal fluidity of mixtures of sodium and potassium nitrate is greater than that computed from the components of the mixture. The difference is nearly constant for a given mixture, *i. e.*, independent of the temperature; it is greatest for equimolecular mixtures. As the equivalent conductance of these same mixtures was found to be less than the calculated values we have additional evidence that the effect of increased fluidity on the migration velocity of the ions is probably more than neutralized by a diminished dissociation of the mixed salts.

11. The results of this investigation provide a more fundamental experimental basis for the further development of the theory of conduction in fused salts than has been hitherto possible. Although the accumulation of these data is laborious as it involves three independent investigations on density, conductivity and viscosity, all of which are of more than ordinary difficulty if a precision better than a per cent. is desired, it is to be hoped that other contributions to this important and interesting field of electro-chemistry will be made in the near future.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY, August, 1907.



# THE CHANGE OF PHASE DUE TO THE PASSAGE OF ELECTRIC WAVES THROUGH THIN PLATES AND THE INDEX OF REFRACTION OF WATER FOR SUCH WAVES, WITH APPLICATIONS TO THE OPTICS OF THIN FILMS AND PRISMS.

#### BY WM. R. BLAIR.

#### INTRODUCTION.

DROFESSOR A. RIGHI in his Optik der Elektrische Schwingungen describes numerous experiments with short electric waves tending toward the proof of the analogy of these with light waves. The disturbance proceeding from a Righi exciter is analogous to a plane polarized ray of white light, and the different wavelengths, instead of being detected by their color, are known by the dimensions of the receiver which responds to them. Accurate measurements of these wave-lengths are made with either the grating or the interferometer. In addition to Righi's work, Lampa's experiments with grating and spectrometer,<sup>1</sup> Cole's application of Fresnel's formulæ,\* Pierce's measurement of indices of refraction by the interferometer method,<sup>3</sup> etc., all seem to justify the assumption of the analogy above referred to and its use in extending our knowledge of optics as well as in the study of electric waves. The following experiments, upon which work has been in progress for the past two and one half years, and their discussion are in line with this assumption, and, as will be seen by the description of the apparatus, ingenious devices, used here in more or less modified form, have been borrowed from all of the experimenters named.

There is fairly good agreement among the values found for the specific inductive capacity of water, except those by Drude,<sup>4</sup> in the determination of which he used about the same wave-length as that used in the following experiments, and those by Lampa<sup>1</sup> for wave-lengths of 4, 6 and 8 mm. In both of these cases the values given

for the index of refraction increase with the decrease in the length of wave used, apparently indicating anomalous dispersion. Drude's measurements were with waves on wires; Lampa used a 4° prism. Drude<sup>5</sup> has treated these results theoretically, adapting the theory of dispersion from Chapter V. of his text-book on the Theory of Optics. His explanation is not easy to accept when the extremely slow frequencies of even the shortest electric waves used compared with those of light waves are taken into consideration.

In his work on the Indices of Refraction of Metals,<sup>6</sup> in which he uses thin metallic prisms, Professor A. Kundt passes the subject of variable change of phase with the remark that "If the refracting angles are correctly measured by reflection, the observations of deviation can hardly be falsified by variable change of phase."

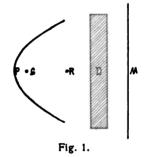
All work in which optical methods are used on the thickness of thin liquid films has been done on the assumption that n, the index of refraction, as computed by the usual formulæ is the same for any thickness of the dielectric. The assumption that n for a given wavelength does not vary with the thickness of the plate is probably correct, but since, as will be shown later, the change of phase is not a linear function of this thickness, other than the usual formulæ must be employed for computing n from the experimental data. The experiment upon the paraffin plates was taken up with the hope of testing the existence of this "variable change of phase," but the apparent failure to get positive results led to the setting aside for the time of the problem.

Although the results of Mr. Cole's<sup>2</sup> attempt, in which he used electric waves of 5 cm. length, to get measurable effects through a plane parallel plate of water gave little hope of success, the object at first of the experiment with water was to determine its index of refraction n by the interferometer method. The finding of different values of n, when computed by the usual formulæ, for different thicknesses of the plate led to further work, the additional purpose of which was a quantitative determination of the variable change o phase.

## Part I.

In the process of repeating some of the work already done with electric waves, a fairly reliable interferometer of essentially the form used by G. Pierce,<sup>3</sup> of Harvard, was set up. Fig. 1 shows the arrangement of this interferometer. It will be noted that the receiver R is influenced by the direct radiation from the gap G as well as by the parallel rays from the parabolic cylinder P, and by the energy reflected from the dielectric D as well as by that reflected from the plane mirror M. The direct radiation from G is a constant as is also the energy reflected from D provided its position remain unchanged during the experiment upon it. The wave-length

used was 15.2 cm. An electrolytic interrupter of frequency above 2,000 was used which, while it was not as constant as could be desired, gave steadier galvanometer deflections and considerably more energy than the ordinary vibrator. The plane mirror Mis movable parallel to itself. The galvanometer used was a four-coil instrument of the Thomson type. Galvanometer readings are taken for different positions of the mirror,



which when plotted give a sinusoidal curve. The maxima and minima of this curve are due to the interference of the reflected with the incident radiation and the distance between any two minima is half a wave length. The introduction of the dielectric D moves these maxima and minima up a distance depending upon its index of refraction and thickness. It is not always possible to recognize a given maximum or minimum after it has been displaced. This necessitates an assumption as to the number of half wave-lengths it has been moved up and consequently a previous rough determination of the index of refraction. For work to which it is well adapted this apparatus is capable of duplicating results to one per cent.

Conversation with Professor Millikan at this time (June, 1905) as to the possible uses to which this apparatus might be put, suggested among other things the problem of the change of phase due to thin films. This problem, it seemed, could easily be experimentally treated for electric waves of 15 or 20 cm. length, since the chief difficulty of the optical treatment, *i. e.*, getting a sufficiently thin and uniform film of known thickness, disappears for this wave-length. Work was accordingly begun with paraffin as the dielectric. Previous work with a prism gave 1.47 for the index of refraction of paraffin. This value is the mean of five determinations, the highest of which is 1.48, the lowest 1.46. The prism had a refracting angle of 60°. Each face was 50 cm. wide by 20 cm. high. The same paraffin used in the prism was used in the interferometer experiment.

Ten plane parallel plates of the order of  $\lambda/10$  in thickness and a plane parallel block of thickness approximating a wave-length were made as follows : (1) Sufficient paraffin for all castings was melted in one vessel; (2) as soon as possible after pouring the molten paraffin into the form, it was immersed in a salt-ice-and-water freezing mixture; (3) using a plane surface, a straight edge, and a carpenter's plane, the castings were made into plane parallel plates. The plates were large enough to extend 2 cm. each way beyond the opening of the parabolic cylinder. This opening was 30 by 31 cm. Their thicknesses in millimeters as measured by means of a pair of outside calipers was as follows :

Plate No.	Meas'd Separately.	Meas'd Together.	Means.
1	8.0		
2	7.5		
3	7.9		
4	5.8		
5	7.3		
Totals nos5.	36.5	37.1	36.8
6	7.5		
7	6.3		
8	6.5		
9	6.4		
10	5.0		
Totals nos. 1-10.	68.2	69.4	68.8
Block.	63.6		63.6

These plates were mounted 1.25 cm. apart. Two measurements



## THE CHANGE OF PHASE.

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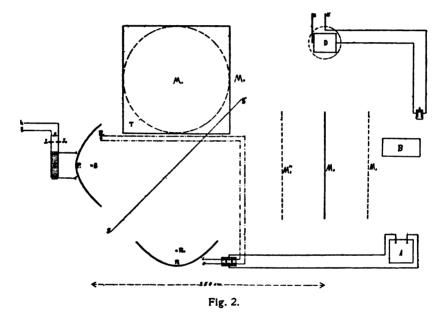
Since the difference between these values and those obtained by the spectrometer method as well as that between the block and the plates might possibly be due to the fact that the thinner plates freeze under somewhat different conditions from the thicker, a change of phase could hardly be argued from this data alone.

Further experiment with the same apparatus showed that a sufficient effect could be obtained through 4 cm. of water to determine its index of refraction, provided an assumption, n = 80, were made as to the number of half wave-lengths a given minimum in the curve showing the interference effect was moved up when the dielectric was put in place.

In order to avoid the necessity of this assumption, a vessel was made of which one of the sides was movable parallel to itself by means of a screw of 11 threads per inch (2.3 per cm.). The plan was to move the plane mirror so as to keep the path of the waves in air constant and, by varying the path in water, to find the wavelength in water. The resulting interference curve was apparently quite irregular but could be qualitatively repeated. The position of its first maximum and minimum indicated a considerably shorter wave-length in water at I.I and 2.I 22ds of an inch (I.3 and 2.4 mm.) than that given by the assumption of  $n^2 = 80$  at 17° C. This variation could not be followed with certainty farther than the first maximum and minimum and that far only qualitatively on account of irregularities evidently due to other causes. A possible variation in the amount of the reflected energy with the thickness of the water plate suggested itself and made some other form of interferometer desirable.

On consideration of these results, Professor Michelson thought further pursuit of the experiment with more elaborate apparatus worth while, suggested the trial of other forms of interferometer, and advised that paraboloids instead of parabolic cylinders be used as reflectors.

this screen a number 22 copper wire was thrown over the heads of tacks at the top and bottom of a wooden frame. After a few trials the wires were put 5 cm. apart. The movable plane mirror  $M_3$  is a circle 122 cm. in diameter. It is mounted on parallel ways and moved by means of a screw of millimeter pitch and 131 cm. in length. On the other arm of the interferometer, an elliptical plane mirror.  $M_1$  122 cm. wide and 173 cm. long, is set at an angle of 45° with the vertical and throws the radiation down through the liquid dielectric to a horizontal reflector  $M_2$ . All reflectors, except



the horizontal ones on which zinc was used, are made of wood covered with a heavy grade of tin foil. Care was taken in their construction to get them plane and to guard against warping.

The path of the waves through this interferometer from gap to receiver is about 6 meters — so great that when the wave producing and receiving apparatus which had given galvanometer throws as desired up to 30 cm. in the old interferometer was installed in this, the largest deflection obtainable at a meter distance in the maximum of the interference effect was 5 cm. While the energy furnished was sufficient to show the interference and measure the

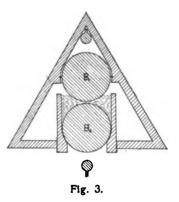
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wave-length, no effects at all could be obtained through water. After two or three months of experimenting, the following apparatus and methods of manipulation were decided upon as satisfactory, the test being the duplication of results to, in most cases, one per cent., in others, more or less depending on the thickness of the dielectric used.

The spark gap (Fig. 3) consists of two balls of aluminium,  $B_1$ and  $B_{\bullet}$ , so mounted in a triangular frame that the space between them can be filled with oil and their distance apart adjusted to .05

mm. or less if desired. The upper ball was mounted on a spindle so that it could be turned to a freshly polished place without changing its position. The lower one was put in a cup which in turn was fitted into the frame by means of threads of millimeter or half millimeter pitch depending on the diameter of the cup. This cup also contains the oil or other dielectric in which it is desired that the sparking shall take place. It was found how-

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ever that the energy from a spark between freshly polished surfaces diminished quite perceptibly as the surface became worn, and that the spark from the surfaces made rough by sparking, while it was weaker, was a much more constant source of energy. Had it not been for the great number of readings, about 20,000 in all, required by the experiment, the rotation of the balls would not have been necessary.

To adjust the gap the balls were set at some distance apart, say 2 mm, and then moved closer together a given fraction of a millimeter at a time, galvanometer readings being taken at each point. From a plot of the relation between the width of the gap and the energy given out by it, the best width was easily determined. This width was found to vary with the shape of the electrodes producing a given wave-length. For the electrodes used in this experiment, it was found to be about one millimeter. A gap intended for long use was set at a width slightly below that giving the maximum amount of energy. During the taking of readings for the above curve, the plane mirrors were equidistant from the screen and the width of the gap was the only thing about the interferometer which was varied. Vaseline oil was used. The three sizes of balls used were 2, 4 and 8 cm. in diameter. The circuit formed by the two balls about the oil gap was connected by means of two air gaps, each about 7 or 8 mm. wide, with the half inch balls forming the terminals of the secondary circuit of a sort of Tesla coil, which in turn worked on the secondary of a 14-inch induction coil.

The primary of the Tesla coil consisted of 37 turns of bare number 14 copper wire wound on a glass tube 7.5 cm. in diameter and 25 cm. long. A sliding contact was used to vary the induction in this circuit and any desired capacity could be introduced. Any suitable secondary circuit could be slipped inside of this primary. The secondary used consisted of 22 meters of number 19 bell wire wound in a single layer on a glass tube 6 cm. in diameter and 27 cm. long. The connecting wires made this circuit 25 meters in length. For connections see Fig. 2 in which b and b' are the wires coming from the secondary of the induction coil. A current of air was passed through each of the three air gaps, made necessary by these connections, after each reading in preparation for the next. This put the gaps in the same condition before each reading and added materially to the constancy of the throws for any given position of the plane mirrors. Two Leyden jars and 15 turns of the primary were used for the 25 meter secondary.

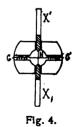
A mercury turbine interrupter run at a frequency of 50 was used in the primary of the induction coil. The  $\frac{1}{12}$  H.P. motor running this interrupter was kept well oiled, and ran on a 110-volt circuit which rarely varied by more than a volt during any set of readings. To secure this constancy of voltage, readings had to be taken between 1:00 and 5:00 A. M., *i. e.*, at the time when there was no variable load on the generator supplying the current. Conditions were also much better at this time for satisfactory use of the galvanometer, the earth's field being almost entirely free from disturbance and the building from vibration. The interrupter itself was frequently cleaned to prevent the possibility of poor contacts due to deposits of either carbon or oxide of mercury on the terminals of the primary inside the interrupter. The primary of the induction coil was further interrupted at D by a pendulum 410 cm. long. This pendulum struck a trigger which put the make and break under control of a spring, insuring not only the same sort of make and break but the same length of contact for each reading of the galvanometer. Experiment with different times and sorts of contacts showed the necessity of such a device as the above and results amply justify its use.

It was thought that preventing the direct radiation from the gap from entering the interferometer added somewhat to the symmetry of the interference curve. This was done by means of a spherical mirror large enough to extend 2 or 3 cm. beyond the gap circuit, and so placed as to have the gap at its focus.

The dividing screen was made adjustable as follows: Number 28 copper wires were fastened at regular intervals to a helical brass wire spring which was slipped over a brass tube. Varying the tension on the spring varied the distance apart of the wires. Each wire is stretched and kept in position by a lead bullet cast on its lower end. A curve is plotted representing the relation between the distinctness of the interference and the distance apart of the screen wires. The distinctness of interference is found by taking the difference between the galvanometer throw at a given maximum and that at the adjacent minimum. The point of maximum distinctness can in this way be determined and the wires set accordingly. The distance apart of the wires in this experiment was from 6 to 7 cm.

Two receivers were used, one of which  $R_1$  was so placed as to receive the direct radiation from the gap; the other  $R_2$  the radiation

after the interference has taken place. These were thermal receivers of the Klemincic type and like those used by Mr. Cole.<sup>7</sup> Fig. 4 shows the construction of a receiver. G and G' connect with the galvanometer. H is the thermal junction. The wires used for the thermal junction were iron and constantan and had a diameter of .001 inch. Round wires of this size could not be obtained from any of the several



compinies applied to for them, consequently the wires were ground down from 3 mill wires. An apparatus for this purpose was constructed which stretched the wire and rotated it at a desired speed. The wire was reduced by the application of fine emery paper. Receivers made from these wires were thought to be more sensitive than those constructed from wires having elliptical sections of the same area. No quantitative test however of this point was made.

X and X', Fig. 4, are copper cylinders which may be slipped off and on the electrodes of the receiver and serve for its tuning. The method of tuning is that described by Mr. Cole.<sup>7</sup> A curve is plotted of readings taken for different lengths over all of the receiver. This curve has but one maximum and it corresponds to that length of receiver best adapted to the gap. Considerable importance attaches to careful tuning if distinct interference effects are desired.

 $R_1$  and  $R_2$  are connected to the same galvanometer so as to oppose each other. The amount of energy received by  $R_1$  may be varied at will by varying its distance from the gap or by changing its dimensions. It is so adjusted that the galvanometer system swings as far to the right at a given minimum due to interference as it does to the left at the succeeding maximum. Several important results are accomplished by this arrangement. Instead of throws varying from 1 or 2 cm. at the minima to 25 or 30 at the maxima, throws of -5 or -6 cm. at the minima and +5 or +6 at the maxima are obtained. A curve plotted from readings of the first sort has a nonsymmetrical appearance, the maxima being sharper and less regular than the minima while for the second sort a smooth sinusoidal curve is obtained in which maxima and minima have the same shape and are alike easily determined. The interference curve is plotted with reference to the line representing the direct radiation from the gap, in this way eliminating to a considerable extent irregularities in the readings due to small variations in the amount of this energy. The extent of a given galvanometer throw is so reduced as to be within the limits for which the throw is proportional to the steady deflection without a sacrifice of distinctness in the resulting plot of these throws.

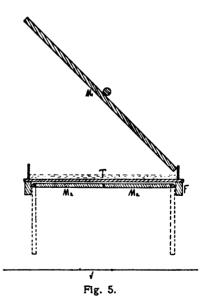
The galvanometer is so adjusted that a throw takes place in a little less than the time of contact as controlled by the pendulum (about 2 seconds), and throws rather than permanent deflections are read because they can be taken more rapidly and with less wear of No. 1.] THE CHANGE OF PHASE.

the gap. In order to reduce these throws to permanent deflections for purposes of comparison, it was planned to determine empirically a plot of the relation existing between a series of throws from 0 up to 25 or 30 cm. and their corresponding deflections. This was done by means of a dry cell and variable resistance in circuit with the galvanometer and the pendulum make and break. The ratio of the permanent deflection to the throw remained constant for wider limits than had been anticipated so that the use of two receivers as described above obviated the necessity of the reduction. The ratio for the galvanometer used was .66. Care was taken in the disposition of coils and lead wires that their magnetic fields should not affect the earth's field at the galvanometer.

Preliminary experiment with the trough for containing the dielectric showed that wood, beeswax and glass reflected enough energy to give quite distinct interference, *i. e.*, their effects could not be neglected in comparison with water or metals and had to be eliminated. It also appeared that the reflection from a thin plate of water varies with its thickness, being greatest at  $\overline{\lambda/4}$  where  $\overline{\lambda}$  is the

wave-length in water assuming n = 8.92; and that on account of variation in the amount of energy transmitted by such a plate with its thickness, the water-beeswax, water-glass, etc., surfaces gave varying reflections.

Elimination of these variable effects was accomplished by the construction of a glass trough and mirrors arranged as shown in Fig. 5, which is a cross-section of the reflectors on this arm of the interferometer.  $M_1$ is the elliptical mirror placed at an angle of 45° to the hori-

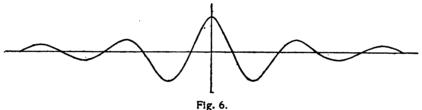


zontal. T is the glass trough 116.75 by 116.70 cm., an almost square bottom, and 10 cm. deep, sides being at right angles to the

7 I

bottom. The bottom of the trough is of selected half inch plate glass, special attention being given to uniformity of thickness and planeness of surface. The sides are of quarter inch glass, also selected plate. The frame F on which the trough rests is mounted on three leveling screws so that, using a delicate level, a sufficiently horizontal surface could be obtained on which to spread uniform plates of the dielectric. The amount of water required for a plate of given thickness was determined to more than the required accuracy by weighing. The  $M_3$ 's are the horizontal reflectors—planes of wood each about 60 by 120 cm., covered with sheet zinc and hinged so that they can be dropped out of the path of the radiation if desired.

The bottom of the trough is 81 cm. from the floor — far enough so that no interference effect could be obtained from the floor within



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the range of the effects being studied. This is easily seen if we consider a characteristic curve of interference (Fig. 6). The highest maximum occurs when the plane mirrors are equidistant from the screen. Four distinct maxima and as many minima may be located on either side of this maximum. Beyond this the effects become less distinct and the curve approaches a straight line. Now (since the distance between two neighboring maxima is  $\lambda/2$ ) for  $\lambda = 20$ cm. the maximum effect due to reflection from the floor would occur at a distance of 20 maxima farther out than the maximum effects due to reflections from the horizontal mirrors.

In what follows the phase change will be defined as the total displacement of a given maximum or minimum of the above curve due to the introduction of the dielectric into the path of the radiation. This has heretofore been, in all work with prisms and on the measurement of thin films, assumed to be a linear function of the thickness of the dielectric. THE CHANGE OF PHASE.

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The method of determining the change of phase due to a given thickness of the dielectric is as follows: (1) Determine the position of the maxima and minima on the interference curve before introducing the dielectric. This requires two sets of readings. The first is taken with the horizontal mirrors in position. In this case the interference is due to reflection of energy from three surfaces — the upper and lower glass surfaces and the zinc surface. The horizontal mirrors are swung down and the second set of readings

Pos.	Throws from H <sub>2</sub> O, Glass and Metal (1).			Throws from H <sub>2</sub> O, and Glass (2).			(1)-(2).	Max. and	Max. and	Phase Change.
	In.	Out.	Mean.	In.	Out.	Mean.	Mi	Min.	in. Min.	
49	-19.0	-18.8	-18.9	- 4.0	- 4.0	- 4.0	-14.9	•	no	
50	-41.8	-37.5	-39.6	-32.0	-28.0	-30.0	- 9.6		H,O	
51	-58.8	-56.0	-57.4	-57.0	-63.0	-60.0	2.6		in	
52	-59.8	53.0	-56.4	-69.0	-86.0	-77.5	21.1	•	Trough.	
53	-55.5	-51.2	-53.3	-82.0	-66.5	-74.2	20.9	52.7	42.8	9.9
54	-44.0	-34.0	-39.0	-52.0	-46.0	-49.0	10.0			
55	-30.0	-29.5	-29.7	-23.0	-25.0	-24.0	- 5.7			
56	-20.5	-25.2	-22.8	- 2.0	- 3.8	- 2.9	-19.9			
57	-29.2	-23.5	-26.3	7.0	10.0	8.5	-34.8	!		
58	-30.5	-32.0	-31.2	- 3.0	- 2.2	- 2.6	-28.6	57.5	47.6	9.9
59	-35.5	-32.0	-33.7	-24.0	-17.8	-20.9	-12.8			
60	-37.0	-35.9	-36.4	-36.0	-37.5	-36.7	.3			
61	-37.0	-33.8	-35.4	-52.0	-58.8	' 55.4	20.0			
62	-40.0	-38.5	-39.2	-72.5	-68.0	-70.0	31.0	62.4	52.4	10.0
63	-40.0	-41.0	-40.5	-51.2	-58.0	-54.6	14.1			
64	-31.8	-33.2	-32.5	-41.5	-40.0	-40.7	8.2			
65	-32.0	-34.0	-33.0	-27.6	-23.7	-25.6	- 7.4	:		
66	-39.5	-40.2	-39.8	-16.0	-10.0	-13.0	-26.8			
67	-36.5	-40.5	-38.5	-16.0	- 7.2	-11.6	-26.9	67.2	57.2	10.0
68	-43.0	-38.0	-40.5	-16.0	- 6.7	'-11.3	-29.2			
69	-36.8	-37.5	-37.1	-24.5	-17.0	-20.7	-16.4	1		
70	-31.5	-31.0	-31.2	-37.5	-30.0	-33.7	2.5	•		
71	-36.2	-34.5	-35.3	-40.5	-46.0	-43.2	7.9	1		
72	-38.0	-35.5	-36.7	-52.0	-60.0	-56.0	19.3	72.1	61.9	10.
73	-33.0	-30.5	-31.7	-48.0	-40.0	-44.0	12.3	1	1	
74	-34.5	-31.8	-33.1	-39.0	-34.0	-36.5	3.4		1	
75	-32.8	-40.0	-36.4	-28.0	-25.5	-26.7	- 9.7			
76	-33.0	-41.0	-37.0	-25.0	-15.0	-20.0	-17.0			
77	-40.0	44.0	-42.0	-20.0	- 9.0	-14.5	-27.5			
	I			I	1	1		1		1.2)10.0
		1	l		1	1	1			8.3

TABLE I.

taken. This set shows interference due to reflection from the upper and lower glass surfaces. Subtracting this second set from the first gives the position of maxima and minima due to reflection from the zinc surface alone. These positions are determined by making a plot of the differences. (2) Introduce a known thickness of the dielectric and proceed as above. This time the first set of readings contains the four elements — reflection from the water surface, the water-glass surface, the lower glass surface and the metal. The second set contains the first three of these elements, and as before subtraction of the second set from the first gives the interference effect due to the energy which has traversed the dielectric to and from the zinc mirror. The maxima and minima are located as before. The phase change is the mean distance between the two sets of positions thus determined.

In this experiment five points were determined for each thickness of the dielectric — the principal maximum and one maximum and a minimum on either side of it. A set of readings is taken as the movable mirror is moved in and out, *i. e.*, toward and away from the screen, through a sufficient distance for the determination of the five positions referred to above. Readings are taken a centimeter apart for a wave-length of 20 cm. more or less for longer or shorter waves. A sample determination of the phase change is shown in Table I. The water-plate is 12 mm. thick and  $\lambda = 19$  cm. in air.

Thickness of Plate in Mm.	l I	2	3	4	5	6	7
Phase Change Thickness of Plate	16.0	16.2	13.4	9.1	8.2	7.2	6.0
Thickness of Plate in Mm.	8	9	10	11	12	13	14
Phase Change Thickness of Plate	6.62	7.10	7.62	8.14	8.33	8.60	8.60
Thickness of Plate in Mm.	15	16	17	18	19	20	21
Phase Change Thickness of Plate	8.10	7.87	7.82	7.69	7.68	7.72	7.85
Thickness of Plate in Mm.	22	23.85	26.5	29.15	31.8	34-45	
Phase Change Thickness of Plate	8.10	8.31	8.03	7.77	7.98	8.07	

TABLE II.

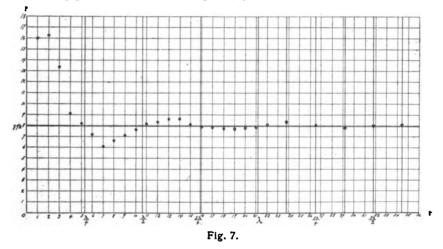
No. 1.] THE CHANGE OF PHASE.

determinations :

Such determinations as the above were made on plates of water of thicknesses varying a millimeter at a time up to 22 mm. and from there varying 2.65 mm. at a time up to 34.45 mm., with a wave-length of 19 cm. The following are the results of these

Fig. 7 shows a plot of these results, the ordinates being the phase change per unit thickness of plate, the abscissæ the thickness of the plate.

It is found that the mean curve crosses the ordinates, t = 5.3, 10.6, 15.9, 21.2, etc., at about p = 7.92. The relation of the index



of refraction n to the phase change per unit thickness of the plate p is given by

n = p + 1

and may be deduced as follows: Let t be the thickness of the water plate, n the index of refraction,  $d_1$  the distance from the screen to the fixed mirror, and  $d_2$  the distance from the screen to the movable mirror. Then

$$d_{1} - t + nt = d_{2}$$

$$(n - 1)t = d_{2} - d_{1}$$

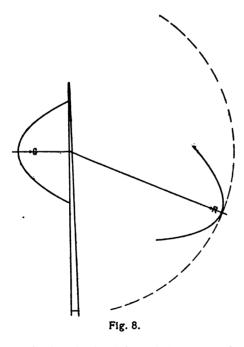
$$n - 1 = \frac{d_{2} - d_{1}}{t} = p$$

$$n = p + 1.$$

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Taking 8.92 as the index of refraction of water and computing the wave-length in water from a mean of its determinations in air, 19.1, it is found that the ordinates, t = 5.3, etc., occur at the quarter wave-lengths.

Since the phase curve continually approaches the straight line, p = 7.92, 8.92 may be taken as the index of refraction of water for thicknesses such that the variation in p is negligible compared with the errors of experiment. At 3.445 cm. or  $13\overline{\lambda}/8$  thickness of the water plate this variation was found to be but little more than the error to which this work is liable. All measurements were made on distilled water at a temperature of about 19° C. No corrections have been made for temperature and variations of  $\frac{1}{2}^{\circ}$ 



or less from this most convenient point have been disregarded. Values of nand K (the specific inductive capacity) for water are usually given for a temperature of  $17^{\circ}$  C. According to the determinations by Heerwagen<sup>8</sup> also by Drude,<sup>4</sup> the correction to be applied for 2 degrees (amounting to about one per cent.) brings the result of this determination to K = 80.4 at  $17^{\circ}$  C.

If the points in Fig. 7 be correctly located, it ought to be possible to construct a prism such that two or more angles of deviation

could be obtained from it by using that part of the prism of thickness 2 mm. to 7 mm. for one determination, 7 mm. to 13 mm. for another, etc., in a spectrometer suitable for this wave-length.

Such a spectrometer was set up (Fig. 8). Two like parabolic cylinders were used for collimating and focusing the rays. The slit afforded by one of these cylinders was 43 cm. wide and 52 cm.

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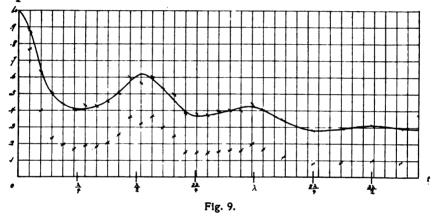
long. In the experiment this width was cut down to 35 cm. and the height to suit the depth of the water in the prism in order that all radiation reaching the focusing cylinder must first pass through the prism. This latter cylinder was attached to an arm pivoted directly below the prism and carried an index which moved over the circumference of a circle of radius 79.2 cm. drawn about the pivot as a center. The prism was 1.3 cm. thick at a distance of 90.3 cm. from the refracting angle which, computed from these dimensions, was about .83°. It was mounted with the face next the collimator perpendicular to the direction of the rays and so that, keeping this face in the same plane, it could be easily moved backward or forward.

Readings were taken as follows: With the empty prism, the focusing cylinder was moved through as large an angle as the mounting would permit (140°) in search of diffraction effects none was found. The single maximum was noted. The prism was then filled with water and the maxima taken; one when the radiation passed through that part of the prism between the points of 2 mm, and 7 mm, thickness and the other between the points of 7 mm. and 13 mm. thickness. In the determination of these maxima, arbitrary divisions were marked on the circumference along which the focusing cylinder moved and the maxima located in terms of these divisions. The maxima were found at 10, 11 and 14, respectively. Measuring the divisions gave the following distances - 10 to 11, 26 mm.; 10 to 14, 106 mm. These distances correspond to 1.9° and 7.7° respectively — the two angles of deviation obtained from the same prism.

A computation of the angle of deviation on the assumption of a uniform change of phase and the index of refraction found above give  $6.6^{\circ}$ . The error in the above determination does not exceed 30'and arises from a lack of sharpness in the maxima. In the work with the paraffin prism the maximum could be found much more accurately.

These results seem to agree well with those given by the interferometer experiment.

To insure accuracy in the location of the points determining the phase curve, it is necessary among other things that the flow of energy from the gap be kept constant only during the taking of each set of readings. Constancy of this factor throughout the entire determination of the curve could not be so nearly realized. It was, however, sufficiently realized to give, in a general way, the relation between the thickness of the water plate and the amount of energy transmitted by it. The lower set of points (Fig. 9) is determined from the curve showing the interference effects due to the transmitted energy. These points have for ordinates the differences in height between the principal maximum and the minima on either side of it, and for abscissæ the thicknesses of the water plate used. It is obvious that since the energy has traversed the plate twice, the square roots of these ordinates, taking that for the plate of zero



thickness to be unity, gives the ordinates of the points on the curve showing the desired relation. This last operation is an approximation, depending on how nearly alike a water-air surface is to a waterglass surface in its reflecting power. As stated above, this curve is only a rough approximation compared to the phase curve, the determination of which was the prime object of the experiment.

It will be seen from this curve of energy transmission that minima occur at the odd quarter wave-lengths and maxima at the even, and that both maxima and minima decrease with the increasing thickness of the plate. The curve is introduced here to show at what points the phase curve is most reliably determined. Where the transmission is least, the maxima and minima of interference effects are not so well defined. Since the quantity p to be determined is the phase change divided by the thickness of the plate, this lack of definition is productive of error in the numerator of the fraction. The error in p is also larger when the denominator of the fraction is small. Consequently the points for thicknesses of from I to 7 mm. are the least accurately determined. From 9 mm. out the error is not more than I per cent. This is of course assuming that no error is occasioned by accident, such as a slight dislocation of a reflector, or a change of level of the trough, which might pass unnoticed during a set of readings. Precautions were taken against such errors and while it is possible, it is not probable, that any occurred. An error of this sort would affect the location of usually one point only, never more than two, since the apparatus was inspected every day and the determination of one point, sometimes two, was all that could be accomplished in that part of the day in which conditions were favorable for taking readings.

Readings have already been taken with wave-lengths of 13 and 35 cm. which do not give accurate quantitative results because of unsatisfactory conditions arising from the necessity of heating the building. The variations of heat and pressure in the steam pipes interfered with the galvanometer and the temperature changes in the dielectric were too great to be neglected. These readings however give, for both longer and shorter wave-lengths, the same sort of curve as described above and apparently point to no change in the value of n in this range of wave-length.

Following out the amount of energy reflected from the water surfaces, it is found as was to have been expected that the maxima of reflection occur at the same points as the minima of transmission and vice versa. The maximum at  $\overline{\lambda}/4$  thickness of the plate is very pronounced, that at  $3\overline{\lambda}/4$  much weaker. It is not probable that there is any variation in the energy reflected from the upper surface of the water, but at the odd quarter wave-lengths this is reënforced by the energy reflected from the water-glass surface while at the half wave-lengths it is cut down by interference. The variation in the amount of transmitted energy has a similar explanation.

The results of these experiments may be briefly summarized as follows :

1. The variation in intensity of both the transmitted and reflected energy is observed to be in accord with the formulæ developed for similar optical effects. These formulæ are found in the texts on optics.

2. The index of refraction of water as determined is 8.92, no indication being given of the anomalous dispersion found by  $Drude^{4,5}$  in the vicinity of the frequency,  $1.5 \times 10.9$ 

3. The change of phase per unit thickness of the dielectric due to the passage of electric waves through thin plates is not a constant for varying thickness of the plate but, when plotted, is a curve crossing the line, p = 7.92, at the quarter wave-length points and having decreasing maxima and minima, the slope at the odd quarters being negative, that at the even being positive. This is clearly shown by the experiment upon water and, if the paraffin in the prism and plates have the same index of refraction, by the experiment upon paraffin.

4. This variable change of phase manifests itself, in the work with the thin prism, as an apparent variation in the thickness of the prism and consequent variation of its refracting angle for different actual thicknesses. This seems to render unreliable all determinations of indices of refraction made with thin prisms, including the work of Kundt on metals and that of Lampa on water. The data obtained by these experimenters is not available for other interpretation than that put upon it by them unless it be known at just what thickness of the prism their observations were made, in addition to the data usually taken in spectrometer experiments.

This experimental work was completed at the Ryerson Physical Laboratory, December 17, 1906. Theoretical considerations, the result of further study of the above data in connection with the author's work at Mount Weather, Va., follow in Part II.

# Part II.

The subject of refraction and reflection of light at the boundary plane between two transparent substances having different indices of refraction has been simply treated by Stokes, who used the principle of reversibility, and more elaborately by Fresnel, who follows the changes undergone by the components of the amplitude in and



perpendicular to the plane of incidence. These treatments are found in the texts on optics. Fresnel's value for that component of the amplitude of the reflected ray which is normal to the plane of incidence is given by

$$R_{n} = -A_{n} \frac{\sin(i-r)}{\sin(i+r)}$$

and for the component in the plane of incidence

$$R_{p} = A_{p} \frac{\tan{(i-r)}}{\tan{(i+r)}}$$

where  $A_n$  and  $A_p$  are the amplitudes of the respective components of the incident ray and i and r are the angles of incidence and refraction. i and r are connected by the relation,

$$\sin i = \pi \sin r,$$

*n* being the index of refraction between the two media which, in this discussion, is taken so that its value is greater than one. If i and r are sufficiently small angles, their sines may be replaced by nr and r and their cosines by 1. Making these changes in the formula gives

$$R_n = -A_n \frac{n-1}{n+1}$$

and

$$R_p = A_p \frac{n-1}{n+1},$$

the values of the amplitudes of the two components for perpendicular incidence.

If the angles r and i are interchanged in these equations,  $R_n$  and  $R_p$  change sign but not numerical value, indicating, as does Stokes' treatment of the subject, that, on reversal of the ray, the same fraction of the light is reflected; but that, if in either case there is no change of phase at reflection, in the other there is a change of phase of  $\pi$ . Fresnel's equations further show on which side of the boundary plane this change of phase occurs for given values of i and n. That  $R_n$  is always negative for n > 1 shows a change of phase of  $\pi$  in this component of the reflected ray for all angles of incidence; that  $R_n$  is positive taken together with its reversal of direction

shows the same thing for values of *i* and *n* such that  $i + r < \pi/2$ . At  $i + r = \pi/2$ , the sign of  $R_p$  changes, indicating no change of phase in the reflected ray for  $i + r > \pi/2$ . It follows that were light incident upon the other side of the boundary plane at such angles that  $i + r > \pi/2$ , there would be a change of phase of  $\pi$  in that component of the reflected ray lying in the plane of incidence. The squares of  $R_n$  and  $R_p$  give the intensities of these components at whatever value of *i* and their sum is the intensity of the reflected ray, while, in accord with the principle of the conservation of energy, the intensity of the light less this sum is the intensity of the light passing through the boundary plane. For values of *n* large, if *n* be taken so that it is greater than one, or small, if taken the other way, the amount of light reflected at the boundary plane is large while the amount transmitted is small and vice versa.

Fresnel's equations have been tested by experiment and very closely represent observed facts. The largest disagreement of observation with theory occurs at the polarizing angle. The change of phase here is not abrupt as the theory indicates, but, while sharp, is continuous, especially if substances having high indices of refraction be used. Surface films have been shown to account in part but not altogether for the disagreement. In testing these formulæ light waves have been used almost altogether. However, assuming their validity for electric waves of 5 cm. length, Mr. Cole has obtained apparently good values for the indices of refraction of water and alcohol, measurements being made of the energy reflected from the surfaces of these liquids.

Using the above well known facts, it is proposed to explain the experimentally determined phase curve described in Part I. of this paper, and related phenomena. The curves of transmission and reflection mentioned in Part I. are incidentally explained.

Fig. 10 represents a cross-section of a film of variable thickness z and having a specific inductive capacity  $K_2$ . It is bounded above and below by dielectrics having specific inductive capacities  $K_1$  and  $K_3$  as shown.  $K_3$  is put into the formula because it nearly always happens that the thin film must be supported by a plate of some other dielectric, which influences considerably the internal reflection of the film. The problem is to determine the phase and intensity



No. 1.]

of the light transmitted by such a film compared with that incident upon its upper surface. Since if there is a change of phase accompanying internal reflection at the boundary planes of this film, it is equal to  $\pi$ , and since, in considering the effect of multiple internal reflections upon either the reflected or transmitted light, two such reflections always occur between the passages of light through a given boundary plane, the total change of phase, not depending on

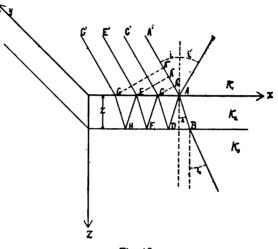


Fig. 10.

s, occurring before the reflected ray returns to the boundary plane in question, is either  $2\pi$  or zero, and no account need be taken of it in this discussion. For this and the further reason that in order to apply Fresnel's equations the amplitude of the incident ray must be resolved into its components in and perpendicular to the plane of incidence, there is no loss of generality in what follows if we consider a simple electromagnetic disturbance of the form,

$$S = A \sin\left(2\pi \frac{t}{T} \pm \delta\right)$$

in either of these planes incident at A. No account need be taken of which of the two planes the disturbance is in and the formulæ deduced will be subject to treatment by either the equation for  $R_n$ or for  $R_p$ , such treatment however giving results peculiar to the plane of the polarized ray, of which the plane of vibration is indicated by the subscript in the equation used. Let *a* be the amplitude of the ray incident at *A*, then *ae*, will be the amplitude of the reflected ray at *A* and  $a(1 - e_1^{2})^{\frac{1}{2}}$ , the amplitude of the refracted ray, where  $e_1$  is a fraction of value depending on  $K_1$  and  $K_2$ . Now if  $a^3$  be the coefficient of transmission and  $\tau$ the distance  $AB = s/\cos r$  through the film of thickness measured in wave-lengths in the film, then  $aa^{\tau}(1 - e_1^{2})^{\frac{1}{2}}$  will be the amplitude of the ray under consideration when it reaches *B*, and  $aa^{\tau}(1 - e_1^{2})^{\frac{1}{2}}(1 - e_2^{2})^{\frac{1}{2}}$ , the amplitude of the refracted ray at *B*. Superposed upon this will be rays of amplitudes,

$$a\alpha^{3r}\epsilon_{1}\epsilon_{2}(1-\epsilon_{1}^{2})^{\frac{1}{2}}(1-\epsilon_{2}^{2})^{\frac{1}{2}}, \quad a\alpha^{5r}\epsilon_{1}^{2}\epsilon_{2}^{2}(1-\epsilon_{1}^{2})^{\frac{1}{2}}(1-\epsilon_{2}^{2})^{\frac{1}{2}}$$

etc., due to rays incident on the upper surface at C, E, etc.  $e_2$  is a fraction of value depending on  $K_2$  and  $K_3$ . If the disturbance incident at A be represented by  $S_1' = a \sin 2\pi t/T$ , that incident at C will be represented by  $S_2' = a \sin 2\pi (t/T + 2\tau \sin^2 r)$ , at E by  $S_3' = a \sin 2\pi (t/T + 4\tau \sin^2 r)$ , etc.,  $2\tau \sin^2 r$  being the distance AA'' in the unit above chosen. It follows therefore that the ray BB' is given by

$$S_{t} = a_{t}' \left\{ \sin 2\pi \left( \frac{t}{T} - \tau \right) + a^{2\tau} \sin 2\pi \left( \frac{t}{T} - \left[ 3\tau - 2\tau \sin^{2} r \right] \right) \right. \\ \left. + a^{4\tau} e_{1}^{2} e_{2}^{2} \sin 2\pi \left( \frac{t}{T} - \left[ 5\tau - 4\tau \sin^{2} r \right] \right) + \cdots \right\} = A_{t} \sin \left( \frac{2\pi t}{T} - \delta_{t} \right)$$

in which

$$A_t \cos \delta_t = a_t' \{ \cos \theta + \alpha^{2\tau} e_1 e_2 \cos (3\theta - 2\varphi) + \alpha^{4\tau} e_1^{2} e_2^{2} \cos (5\theta - 4\varphi) + \cdots \}$$
  
and

 $A_{i} \sin \delta_{i} = a_{i}' \{ \sin \theta + \alpha^{2\tau} e_{1} e_{2} \sin(3\theta - 2\varphi) + \alpha^{4\tau} e_{1}^{2} e_{2}^{2} \sin(5\theta - 4\varphi) + \cdots \}$ where

$$a_{i}' = aa^{\tau} (I - e_{1}^{2})^{\frac{1}{2}} (I - e_{2}^{2})^{\frac{1}{2}}, \quad \theta = 2\pi\tau$$
$$\varphi = 2\pi\tau \sin^{2} r.$$

and

To sum these series, substitute in the equation,

$$\frac{1}{1-x} = 1 + x + x^2 + x^3 + \cdots,$$
$$x = a^{2\tau} e_1 e_2 \{\cos \delta(\theta - \varphi) + i \sin (\theta - \varphi)\}$$



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I.

and multiply both members by  $a'_i(\cos \theta + i \sin \theta)$ ; equate the real numbers in one member to those in the other and similarly for the imaginaries; simplify and get

$$A_{i} \cos \delta_{i} = \frac{a_{i}' \left[\cos \theta - a^{2\tau} e_{1} e_{2} \cos \left(\theta - 2\varphi\right)\right]}{1 - 2a^{2\tau} e_{1} e_{2} \cos 2\left(\theta - \varphi\right) + a^{4\tau} e_{1}^{2} e_{2}^{2\tau}}$$
$$A_{i} \sin \delta_{i} = \frac{a_{i}' \left[\sin \theta - a^{2\tau} e_{1} e_{2} \sin \left(\theta - 2\varphi\right)\right]}{1 - 2a^{2\tau} e_{1} e_{2} \cos 2\left(\theta - \varphi\right) + a^{4\tau} e_{1}^{2} e_{2}^{2\tau}}$$
$$\tan \delta_{i} = \frac{\sin \theta + a^{2\tau} e_{1} e_{2} \sin \left(\theta - 2\varphi\right)}{\cos \theta + a^{2\tau} e_{1} e_{2} \cos \left(\theta - 2\varphi\right)},$$

II. 
$$A_i^3 = \frac{(a_i')^3}{1 - 2a^{2\tau}e_1e_2\cos 2(\theta - \varphi) + a^{4\tau}e_1^3e_3^2}$$

Making a similar calculation of the phase change and intensity of reflected light, remembering that there is a difference of phase of  $\pi$  between externally and internally reflected rays, gives

$$A_{r} \cos \delta_{r} = a_{r}' \frac{\cos 2(\theta - \varphi) - a^{2r}e_{1}e_{2}}{1 - 2a^{2r}e_{1}e_{2} \cos 2(\theta - \varphi) + a^{4r}e_{1}^{2}e_{2}^{2}} - ae_{1}$$

$$A_{r} \sin \delta_{r} = a_{r}' \frac{\sin 2(\theta - \varphi)}{1 - 2a^{2r}e_{1}e_{2} \cos 2(\theta - \varphi) + a^{4r}e_{1}^{2}e_{2}^{2}}$$
III.  $\cot \delta_{r} + \frac{ae_{1}}{A_{r}} \csc \delta_{r} = \frac{\cos 2(\theta - \varphi) - a^{2r}e_{1}e_{2}}{\sin 2(\theta - \varphi)},$ 

IV. 
$$A_r^2 = \frac{(a_r')^2 - 2aa_r'e_1[\cos 2(\theta - \varphi) - a^{2\tau}e_1e_2]}{1 - 2a^{2\tau}e_1e_2\cos 2(\theta - \varphi) + a^{4\tau}e_1^{-2}e_2^{-2}} - a^2e_1^2,$$

where  $a_{r}' = a a^{2r} e_{2} (1 - e_{1}^{2}).$ 

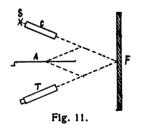
As was to be expected, if  $\alpha$  be put equal to one, *i. e.*, if there be no absorption of radiation by the film,

$$A_{t}^{\prime 2} + A_{r}^{\prime 2} = a^{2}$$

This check upon the work together with the fact that the formulæ  $A_i^2$  and  $A_r^3$  appear in the proper form for direct application to the experimental data is considered justification for deducing them here along with those for  $\partial_i$  and  $\partial_r$  although, in slightly differing forms, they will be found, as noted in (1) of the summary of Part I., in the texts on optics.

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The above formulæ are quite general and simplify considerably under reduction to special cases. As they stand, however, data could be obtained for the determination of A, and  $\delta_{n}$  if the transparent film upon which measurements are to be made were introduced in front of one of the plane mirrrors of an interferometer in such a way that the angle of incidence could be varied. A series of dielectrics could be used to give different values of n. The thickness of the film must always be known and for a given dielectric could be varied. The smaller the absorption coefficient the thicker the films from which measurable effects may be obtained. Such an experiment is practicable if one uses electric waves of convenient length, but the construction of sufficiently thin uniform films for use with light waves and, since the usual optical methods are not available, the measurement of their thickness, makes the problem a difficult one. One method which suggests itself is the construction of one sufficiently thin, uniform film upon which measurements may be taken with different wave-lengths. This film need not be large in extent and may be made from some metal, better from a more transparent substance, having as high an index of refraction as possible, the thickness to be determined by the optical.



method after a suitable wave-length or lengths have been found. Another method is to make three measurements on a given film of either  $\delta_i$  or  $\delta_r$  for different angles of incidence; substitute in the proper formula and solve simultaneously for n, z and a. An arrangement of this sort shown in Fig. I I could be used in the determination of  $A_i$ 

and  $\delta_r$ . S is the source of radiation, C the collimator, F the film, T the telescope or receiver, and A a device for varying the angle of incidence.

No. I.]

# THE CHANGE OF PHASE.

$z$ (in $\lambda$ 's).	$\theta$ (in $\pi$ ).	$\delta_t (in \pi).$	∮ (Calc.).	z (in mm.).	∮ (Obs.).
1 32	.0625	.1436	19.49	1	16.00
IS	.1250	.2474	16.65		
3 <sup>3</sup> 2	.1875	.3144	13.96	2	16.20
18	.2500	.3640	12.00	3	13.40
1 <sup>3</sup> 6	.3750	.4370	9.40	4	9.10
14	.5000	.5000	7.92	5	8.20
				6	7.20
1 <u>6</u>	6250	.5698	7.13	7	6.14
<u>8</u>	.7500	.6633	6.89	8	6.62
7	.8750	.8046	7.20	9	7.10
10				10	7.62
1/2	1.0000	1.0000	7.92	11	8.14
9 16	1.1250	1.1843	8.39	12	8.33
58	1.2500	1.3154	8.39	13	8.60
				14	8.60
11 16	1.3750	1.4132	8.17	15	8.10
$\frac{3}{4}$	1.5000	1.5000	7.92	16	÷7.87
13	1.6250	1.5915	7.74	17	7.82
7	1.7500	1.7009	7.67	18	7.69
8		1.1007		19	7.68
$\frac{15}{16}$	1.8750	1.8389	7.75	20	7.72
1	2.0000	2.0000	7.92	21	7.85
-				22	8.10

TABLE III.

Since  $\delta_t$  is the total change of phase due to the film of thickness z and  $2\pi z/n$  (z is measured in wave-lengths in the film) the change of phase which model are site to film more severely the net change.

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where p is the change of phase per unit thickness of the film as measured experimentally.

From Fresnel's formulæ,

and

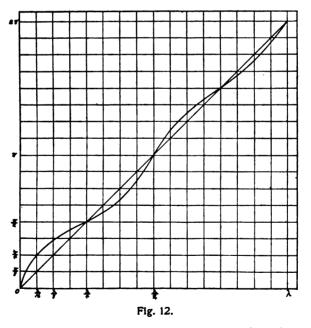
$$e_2 = \frac{n_2 - 1}{n_2 + 1}$$

 $e_1 = \frac{n_1 - 1}{n_1 + 1}$ 

where  $n_1$  is the index of refraction of water with reference to air, 8.92, and  $n_2$  is the index of water with reference to glass, 3.38; 2.64 is taken as the index of refraction of glass. Evaluating these gives

$$e_1 = .798,$$
  
 $e_2 = .543.$ 

A computation of  $\alpha^3$  from selected ordinates of the phase curve gives a value of about .31, which indicates that over 60 per cent. of



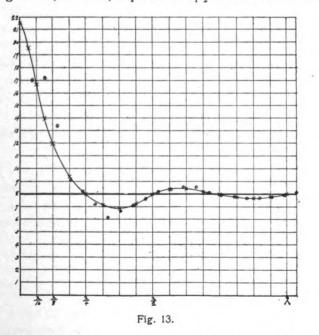
the energy of radiation is absorbed by one wave-length, 21.2 mm., thickness of water.

Table III. shows the values of  $\delta_i$  and p as calculated from the



### No. I.] THE CHANGE OF PHASE.

formulæ up to z = 1 and, for comparison, the observed values of p. The curve shown in Fig. 12 is the graph of  $\partial_{p}$ , the diagonal giving the values of  $\theta$ . Fig. 13 shows the observed and calculated values of p. Observed values are marked  $\odot$ , calculated  $\times$ . The agreement is good with the exception of the third, seventh and fourteenth points. It is evident that the departure of the curve in Fig. 12 from the straight line,  $\theta = 2\pi z$ , depends on  $e_1 e_2$  unless the coefficient of



transmission be much less than one. This departure is considerable even with low indices of refraction, as will be seen from the application of the formulæ I., V. and VI. to the experiment on the paraffin plates described in Part I.

Take 1.47 as the index of refraction of paraffin and assume the coefficient of transmission to be one. There can be little error in this assumption even though  $a^2$  be considerably less than one since

and the mean index of refraction for plates of the above thickness computed by V. and VI. is

$$n = 1.565,$$

an increase of almost  $6\frac{1}{2}$  per cent. over 1.47. The block of paraffin has a thickness of  $\frac{3}{5}$  of a wave-length. Applying the formula to this thickness gives the index to be

$$n = 1.484$$

or nearly 1 per cent. over 1.47.

While the results of this experiment on the paraffin plates did not at the time, August, 1905, seem to justify the assertion that the differences in the different determinations of the index of refraction were due to a change of phase not a linear function of the thickness of the plate, these theoretical considerations appear to show that such was the case.

The application of the above formulæ, being fairly well justified by experiment, may further be made to the work of Johonnott<sup>9</sup> and others on the thickness of thin liquid films. For an index of 1.33, neglecting the coefficient of transmission and assuming perpendicular incidence, formula I. becomes approximately

$$\tan \delta_i = \frac{1.02}{.98} \tan 2\pi z.$$

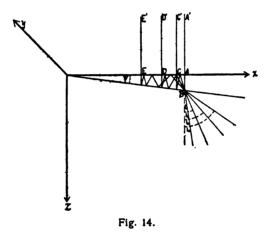
Recomputing from Johonnott's data in a case in which he gets  $z\lambda = 12.6 \,\mu\mu$ , and taking the phase change into consideration gives  $z\lambda = 12.1 \,\mu\mu$ , the difference being about 4 per cent. The mean of  $12 \,\mu\mu$  as limiting thickness of the first block becomes  $11.5 \,\mu\mu$ .

It is probable that this correction just accounts for the difference in the two values found by Reinold and Rücker<sup>10</sup> for this same quantity and justifies the latter of the following assumptions. They used two methods in their determinations : an optical method based upon the assumption that the index of refraction as computed by the usual formulæ is the same for any thickness of plate and an electrical method underlying which was a similar assumption with reference to the resistance of a liquid. By the first method they obtain 11.8  $\mu\mu$ , by the second 11.3  $\mu\mu$ .



The spectrometer experiment described in part I. was intended to serve as a check on the work with the interferometer. While it serves this purpose well, the formulæ used in the interpretation of the results with thin plates cannot, except in a general way, be used to account for the results with the thin prism.

Fig. 14 shows a section of the prism and the paths of the rays through it. This figure illustrates the special case in which incidence is perpendicular,  $\psi$  is .83° and *n* is 8.92. The consideration of the general case has not been found profitable on account of the comparatively complicated expressions which arise, and its limited application to special cases. The angle of incidence  $r_1$  of the ray



AB on the second face at B is  $\psi$ . Its angle of refraction  $i_1$  is  $7^\circ + 25'$ . For the ray CB,  $r_2$  is  $3\psi$ ,  $i_2$  is  $22^\circ + 48'$ ; for DB,  $r_3$  is  $5\psi$  and  $i_3$  is  $40^\circ + 12'$ ; for EB,  $r_4$  is  $7\psi$  and  $i_4$  is  $64^\circ + 40'$ . Total reflection takes place at  $7\frac{3}{4}\psi$ .  $i_3$  and  $i_4$  are so large that the refracted parts of DB and EB could not enter the focusing cylinder at the same time as the refracted parts of AB and CB provided the cylinder be at the position for the maximum effect of the radiation upon the receiver as determined by the experiment. The rays AB and CB are therefore the only ones to be considered. It is clear that a circular cylinder of appropriate curvature would have given a better focus of the diverging rays and consequently a better defined maximum than that given by the parabolic cylinder used.

The resulting disturbance at B due to AB and CB is given approximately by

$$S = s_1 + s_2$$
  
=  $A \sin\left(2\pi \frac{t}{T} - \delta\right)$   
=  $.3614aa^{x \tan \psi} \sin 2\pi \left(\frac{t}{T} - x \tan \psi\right)$   
+  $.226aa^{3x \tan \psi} \sin 2\pi \left(\frac{t}{T} - 3x \tan \psi\right)$ 

where  $\alpha$  is the amplitude of the rays incident at A and  $\alpha^3$ , the coefficient of transmission. Fresnel's formulæ are again used in getting the values of e. x is measured in wave-lengths in water. Putting  $\theta$  for  $2\pi x \tan \phi$  and solving gives

$$\tan \vartheta = \frac{1.6 + 3a^{\tau} - 4a^{\tau}\sin^2\theta}{1.6 - 3a^{\tau} + 4a^{\tau}\cos^2\theta}\tan \theta.$$

Table IV. gives a few of the values of  $\tau$ ,  $\theta$  and  $\delta$  for comparison.

$\tau$ (in $\lambda$ 's).	0 (in *).	( n <del>s</del> ).	$\tau$ (in $\lambda$ 's).	0 (in π).	δ (in π).
4	.0625	.1093	76	.8750	.8093
4	.1875	.3157	i	1.0000	1.0000
ł	.2500	.4076	16	1.1250	1.1836
Å	.3750	.4650	4	1.2500	1.3430
ł	.5000	.5000	<b>11</b>	1.3750	1.4688
18	.6250	.5075	l i	1.5000	1.5000
4	.7500	.6281	1	1.6250	1.5604

TABLE IV.

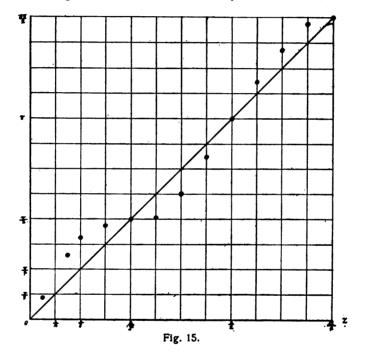
Fig. 15 is a graph of these values and makes apparent the reason for the different angles of deviation found for different parts of the same prism. The values of  $\delta$  are marked  $\odot$ . They have a somewhat similar relation to  $\theta$  as that shown in Fig. 12, values of  $\theta$  being given by the diagonal straight line. A computation of D, the angle of deviation, for that part of the prism from  $\frac{1}{8}\lambda$  to  $\frac{5}{16}\lambda$  in thickness gives

$$D = 1^{\circ} + 45.5'.$$

This value is 8.5' less than the value observed for D at approximately this part of the prism. A similar computation gives

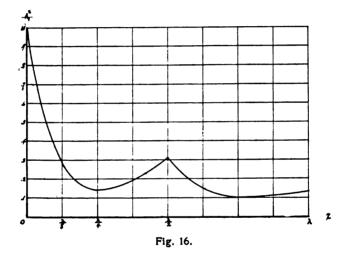
$$D = 8^{\circ} + 33'$$

for that part of the prism between  $\frac{5}{16}\lambda$  and  $\frac{1}{16}\lambda$  in thickness. This value is 51' greater than that observed for about the same part of the prism. Both experiment and calculation on the thin prism are somewhat rough but of sufficient accuracy to show that, for a thin



prism of material the index of refraction of which differs much from one in either direction, the angle of deviation is different for different parts of the prism and cannot be used in the ordinary formulæ for computing the index of refraction from data obtained by means of a spectrometer.

Fig. 16 shows the curve of transmission of energy as worked out from formula II. for a thin film. This curve is below the observed curve. It has sharp maxima and broad minima compared with that in Fig. 9, which taken with the curve in Fig. 6 seems to indicate that the receiver responds to a limited group of wave-lengths in the vicinity of the one wave-length to which it is tuned. Further evidence is had in the fact that, when no water plate intervenes, the wave-length responded to by the receiver is quite uniformly 19.1 cm. in air, while, with the plate intervening, wave-lengths varying from this by several millimeters are obtained as in the sample set of readings given in Part I. This disagreement between the curves in Fig. 16 and Fig. 9 is due no doubt to the fact that the curve in Fig. 16 is computed for one wave-length only, while that in Fig. 9 is the resultant effect of a limited group of wave-lengths. Where the plate is almost opaque to a given



wave-length, it is transparent to others either longer or shorter. The pulse from the gap containing a given group of component wave-lengths has some of these lengths sorted out by the plate so that a slightly different group presents itself to the receiver at every thickness of the plate. The receiver, having been tuned to the original group, responds less energetically to the modified groups; this response being in the nature of a compromise between the wave-lengths offered by a given group and the ability of the receiver to respond to them.

It follows that at any given thickness of plate certain wavelengths, given by  $\tau = (2n - 1)\lambda/4$  are partially taken out of the

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# THE CHANGE OF PHASE.

group, while others given by  $\tau = n\lambda/2$  are more intense. For thin prisms, Fig. 15 shows the same sort of selection. The prism becomes a sort of transmission grating. It is seen further that a prism having a given refracting angle and composed of material having a given index of refraction will produce for a given angle of incidence an angle of deviation depending upon the wave-length. Consider in Fig. 15 the part of the prism between  $z = \frac{5}{16}$  and  $z = \frac{1}{16}$ . For a given wave-length  $\lambda$  in the medium of the prism, the distance along the face of the prism will be d, for any other wave-length  $\lambda'$ , the distance d' will be greater or less than  $\lambda$  depending on whether  $\lambda'$  is greater or less than  $\lambda$ , but the change in phase between these two thicknesses will be the same, since z is measured in wave-lengths in the prism. This means that for the shorter wave-lengths the virtual face of the prism will make a greater angle with the real face at that part of the prism where, for the wave-length under consideration, the transmitted light is most intense, with the result that the angle of deviation of the shorter wave-length will be greater. Lampa's1 experiment on the index of refraction of water seems to support this conclusion. He used a prism having a refracting angle of 4° and found the angles of deviation for the three wave-lengths, 4, 6 and 8 mm. The groups of wave-lengths in which these predominated were probably quite From these angles he computed, by the usual formula, limited. the following values of the specific inductive capacity of water :

$$K_{(\lambda=4)} = 90.2,$$
  
 $K_{(\lambda=6)} = 88.4,$   
 $K_{(\lambda=8)} = 80.4.$ 

Professor A. Kundt,<sup>6</sup> in his experiments on thin metallic prisms, made two measurements on each prism. (1) Its refracting angle. This was measured by the reflection from the face of the prism. If

made from which the thickness of the prism at the part in question can be determined, consequently a simultaneous computation, assuming the above formulæ to hold for metals, of the actual angles of refraction and deviation is impossible.

At what refracting angle the virtual face of the prism coincides with the real face must be somewhat dependent upon the adjustment of the other parts of the spectrometer and is a subject for further experiment. A theoretically correct method of determining the index of refraction of a material for a given wave-length  $\lambda$ , is to use a plane parallel plate of it of thickness  $n\lambda/2$  and measure the retardation of the light due to its passage through this plate. n is a whole number and  $\lambda$  is the wave-length in the material used. Practically n need not be a whole number if the plate be thick when measured in wave-lengths.

To the summary given in Part I. may now be added :

5. The variable change of phase observed in the experiments with thin films and prisms also the variation in intensity of the transmitted and reflected energy are interference phenomena and are due to the superposition of the successive transmissions or reflections arising from multiple internal reflection.

6. The text-book formulæ used for computing the index of refraction of a substance from data taken with either the interferometer or the spectrometer will not apply in the cases of thin films and thin prisms but must be supplemented by the formulæ given above.

7. The virtual face of a thin prism is not coincident with its real face but, for a given wave-length in the medium of the prism, a section perpendicular to the edge shows a somewhat sinusoidal curve which cuts the real face at those points where the thickness of the prism is  $n\lambda/4$ . Its slope is least at the points  $(2n - 1)\lambda/4$ , greatest at  $n\lambda/2$ , these slopes being steeper for wave-lengths shorter than  $\lambda$  and less steep for those longer. The transmitted energy is least at  $(2n - 1)\lambda/4$ , greatest at  $n\lambda/2$  and is always dependent upon the index of refraction. The thin prism is thus a transmission grating possessed of properties by which to a certain extent, it accomplishes the analysis and dispersion of white light.

For their helpful criticism of his work and the suggestions above

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mentioned, the author takes this opportunity of expressing his appreciation to Professors Michelson and Millikan.

MOUNT WEATHER OBSERVATORY,

BLUEMONT, VA., October 9, 1907.

#### BIBLIOGRAPHY.

The numbers to the right and above the names of the authors and articles mentioned in this paper refer to the following;

I. A. Lampa, Annalen der Physik, 61.

2. A. D. Cole, Annalen der Physik, 57.

3. G. Pierce, Phil. Mag., I, series 6.

4. P. Drude, Annalen der Physik, 58 and 59.

5. P. Drude, Annalen der Physik, 64.

6. A. Kundt, Phil. Mag., 26, series 5.

7. A. D. Cole, PHYSICAL REVIEW, Vol. 20, No. 4.

8. F. Heerwagen, Annalen der Physik, 48 and 49.

9. E. S. Johonnott, Phil. Mag., 47, series 5.

10. Reinold and Rücker, Phil. Trans., Vol. 184 (A).



# THE VISCOSITY OF WATER AT VERY LOW RATES OF SHEAR.

### BY L. E. GURNEY.

# INTRODUCTION.

THE following investigation was carried out at the suggestion of Professor Albert A Michael Professor Albert A. Michelson in the spring and summer of 1906 at the Ryerson Physical Laboratory of the University of Chicago. I desire to thank him and to thank Professor R. A. Millikan for their continued interest and helpful advice during the course of the work.

It was undertaken to test certain conclusions arrived at by Professor A. W. Duff,<sup>1</sup> which seemed quite remarkable if true. These conclusions (discussed later in this paper) were not verified and the work was extended to the measurement of the coefficient of viscosity of water at lower rates of shear (5.28 to .663 radians per second) than had hitherto been used. The main purpose was to determine if posssible whether its value changes as the motion of the liquid becomes very slight - a point of considerable theoretical interest in a study of the nature of liquids.

The method employed was, with a number of changes, similar to that used by Couette<sup>2</sup> and others. The liquid was enclosed between concentric cylindrical walls; the outer cylinder was turned at a known rate about its axis; the inner cylinder was held fixed by a couple of known value; hence the coefficient of viscosity of the fluid could be found.

This method has not previously been used, as far as I know, with very low rates of shear yet it offers peculiar advantages. (1) With

tion was not set by any inherent mechanical difficulties in the construction of apparatus but by other causes. (2) All parts of the liquid are sheared at somewhat nearly the same rate (see Fig. 3) and continually at the same rate. In the method of flow through tubes the rate of shear varies from O at the axis of the tube to a maximum at the walls; in the method of oscillating discs or spheres all parts of the fluid are sheared at rates which vary from O to a maximum at different times. This lack of uniformity seems objectionable in an investigation upon the constancy of the viscosity coefficient at low rates of shear.

GENERAL OUTLINE OF METHOD AND THEORY.

The Experiment. — All the constants of the apparatus having been determined the routine work of the experiment fell easily into two parts. No mention is made here of details.

1. A small cylinder was suspended by means of a steel wire centrally within a larger cylindrical vessel, both cylinders being vertical. Then before any liquid was placed in the apparatus the inner cylinder was set into oscillation and its period of free rotation about its suspension measured.

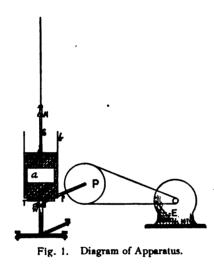
2. The outer cylinder was filled with water until the inner one was submerged to the proper depth and was then made to rotate slowly at a uniform rate. On account of the viscosity of the water this caused the inner cylinder to deflect through a small angle until it was balanced by the torsion of the wire; this angle, the speed of rotation and the temperature of the water were then determined.

The second part was then repeated using an inner cylinder of about the same diameter but twice as long as the preceding one. This furnished data from which the effects due to the ends of the cylinders could be eliminated.

Apparatus. — The essential parts of the apparatus are shown in the accompanying diagram (Fig. 1).

A cylindrical vessel b with a flat bottom, constructed of heavy brass tubing, 22 cm. in height, 11 cm. inside diameter, rested upon a turn-table T. The surface of the table was a plane at right angles to its axis of rotation and could be made horizontal by three leveling screws in its tripod base. To insure uniform motion at the small angular velocities used, the table was rotated by a worm-gear W joined by a flexible shaft F to a pulley P. This pulley, in turn, was connected by light leather belting to a small electric motor E. The worm-gear W reduced the angular velocity of the pulley one hundred times and by using pulleys of different diameters all desired velocities were communicated to the turn-table.

Two inner cylinders were employed similar to a and about 9 cm. in diameter — one about 5 cm. and the other about 10 cm. in length. They were made of brass tubing and had plane brass ends pierced



above and below by two very small holes; they were hollow and when immersed were filled with water which passed through these holes. A small brass rod S passed through the ends and along the axis of each cylinder. This rod or stem was 25 cm. long in each case; its lower end terminated at the bottom of the cylinder and its upper end was provided with a screw clamp for attaching it to the suspension. When either of the cylinders was in place as at a its

lower end was 5 cm. above the bottom of the outer cylinder, its top was immersed under 5 cm. of water and about 8 cm. of the stem projected above the outer vessel. A small mirror M was attached to the top of the stem and the deflections of the inner cylinder were observed with the aid of a telescope and curved scale placed at a distance of 2.5 meters.

The suspensions used were small steel wires. The upper ends were clamped into jewelers' chucks held in a heavy steel frame. The lower ends were fastened into the stems of the cylinders by screw clamps. The properties of these suspensions are described in more detail later.

Temperatures were measured by thrusting into the water an ordinary laboratory thermometer graduated to tenths of degrees. This

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thermometer was compared with the Baudin Standard No. 15,170 and found to have a correction of +.17° through the range of temperature used.

Time intervals were usually of several minutes duration and were usually measured by a stop watch, wound up to the same tension before each observation and frequently calibrated; it was found to have a very constant rate. Intervals requiring more accuracy were measured by direct reference, through electrical contacts, to a standard astronomical clock.

Freshly distilled water was used from which the air had been removed by boiling or the vacuum process although this precaution did not seem especially necessary.

All the apparatus was finally installed in a room without windows and with double doors, whose temperature could, by means of an electrical device, be kept constant within a tenth of a degree as long as might be desired. The temperature of the water was not equally constant inasmuch as a certain amount of evaporation at its surface could not be avoided. But these changes were slow and small in amount and there is no reason to fear error from this source,

Expression for the Coefficient of Viscosity. — From the equations of Navier,<sup>1</sup> together with the equation of continuity, it may be shown that a cylinder of radius b, rotating with constant angular velocity  $\omega$ , will exert upon an inner, fixed, concentric cylinder of radius a (the space between them being filled with a liquid whose coefficient of viscosity is  $\eta$ ) a couple I given by the relation

I. 
$$\Gamma = 4\pi\eta l \frac{a^2b^2}{b^2 - a^2}$$

where *l* is the common length of the two cylinders and the effects due to their ends is disregarded.

If now the inner cylinder be suspended by a wire (length L, radius

Now if some body whose moment of inertia M is known be suspended upon this wire and oscillate freely about it with a period T we have a third and familiar relation

III. 
$$T = 2\pi \sqrt{\frac{M}{\frac{1}{2}\pi n r^4/L}}.$$

Eliminating I and the quantity  $m^{4}/L$  from these three equations we obtain

IV. 
$$\eta = \frac{\pi \varphi M(b^2 - a^3)}{a^2 b^2 l^2 \omega l}$$

where  $\eta = \text{coefficient of viscosity of the liquid}$ ,

 $\varphi$  = angular displacement of the inner cylinder,

M = moment of inertia of chosen body about suspension,

T = period of free oscillation of body about suspension,

a =radius of inner cylinder,

l =length of inner cylinder,

b =radius of outer cylinder.

In this investigation the angle  $\varphi$  was determined by a mirror and scale and the shorter of the inner cylinders was the body chosen for determining the constants M and T. Bearing this in mind the last equation may be written in the more convenient form

V. 
$$\eta = \frac{stK}{dT^2}$$

where d = distance of scale from mirror,

 $s = 2\varphi d$ , the observed deflection of scale image,

 $t = 2\pi/\omega$ , the time of one revolution of outer cylinder,

 $K = M(b^2 - a^2)/4a^2b^2l$ , a constant depending only upon the dimensions of the cylinders.

Shearing in the Liquid. - Couette (loc. cit.) gives an expression



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From this expression  $S_r$ , the rate at which the liquid is being sheared at a distance r from the axis, may be found.

Let  $X_0$  and  $Y_0$  (see figure) be two points in the liquid on a common diameter of the cylinders at distances r and  $r + \Delta r$  from the axis and suppose that in the time  $\Delta t$  they advance to the positions X and Y. Then we have

$$S_{r} = \lim_{\Delta r \doteq 0} \left[ \frac{\overline{YZ}}{\overline{XZ}} / \Delta t \right]$$
$$= \lim_{\Delta r \doteq 0} \left[ \frac{(r + \Delta r)(\omega_{r+\Delta r} - \omega_{r})}{\Delta r} \right]$$

by substitution from Eq. VI. this takes the form

$$S_r = \lim_{\Delta r \doteq 0} \left[ \frac{a^2 b^2 (r + \Delta r)}{b^2 - a^2} \left( \frac{(r + \Delta r)^2 - r^2}{r^2 \Delta^2 r (r + \Delta r)^2} \right) \omega \right]$$
  
VII. 
$$= \frac{2a^2 b^2 \omega}{r^2 (b^2 - a^2)}.$$

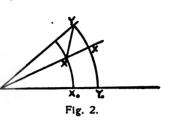
Z

It appears from this equation that if the distance between the cylinders be fairly small compared with their radii that the liquid will be sheared at a fairly uniform rate all across the ring. Fig. 3 shows the relative rate at which different parts of the liquid were sheared in these experiments. The curve is the same for all velocities of rotation of the apparatus.

The average rate S at which the whole mass of the liquid is being sheared may be found from Eq. VII. by multiplying each element of a cross-section by its rate of shear and dividing the sum of these products by the area of a cross-section since they are all alike. This gives

$$S = \frac{8a^2b^2\omega}{\pi(b^2 - a^2)^2} \int_0^{\pi/2} d\theta \int_a^b \frac{d\mathbf{r}}{\mathbf{r}}$$
$$= \frac{4a^2b^2\omega}{(b^2 - a^2)^2} \log \frac{b}{a}$$

VIII.



Correction for End Effects. — Equations IV. and V. apply only to the case of an ideal cylinder without ends. The effect due to the ends of the real cylinders necessarily used in practice might be allowed for either by the calculation of another term in these equations or by experimental means. Couette eliminated it by continuing the inner cylinder with fixed guard cylinders. In this investigation it was eliminated by the successive use of two cylinders of approximately the same radius but of different lengths. If the same conditions prevail about the ends of both cylinders it may be assumed that the effect due to them will be the same in either case

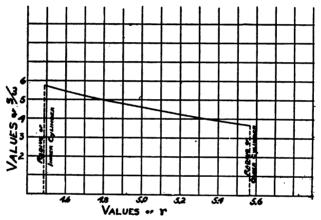


Fig. 3. This curve represents the relative rates of shearing at different parts of the liquid as one passes from the inner to the outer cylinder. It is the same for all velocities of rotation. The equation of the curve is equation VII. where the constants are given the values they had in this investigation.

and may therefore be eliminated by subtraction. In this way may be obtained the deflection due to an ideal cylindrical surface whose dimensions are calculable if we know those of the two real cylinders.

Dimensions of the Ideal Cylinder. — We will make three assumptions: (1) That the deflection of the ideal cylinder is equal to the difference between the deflections of the two real inner cylinders. (2) That its length equals the difference between their lengths. (3) That the effect due to the ends is the same for each of the real cylinders.

It remains to find the radius of the ideal cylinder. Obviously it would be the same as the radii of the real cylinders if they were strictly equal to each other but since this condition was only approximately fulfilled it is necessary to proceed as follows:

Let s be the deflection produced by the ideal cylinder, a its radius, l its length.

Let  $(s_1, a_1, l_1)$  and  $(s_2, a_3, l_3)$  be the corresponding expressions for the longer and shorter real inner cylinders.

Let  $s_{\mathbf{B}}$  be that part of the deflection of each real cylinder due to its ends.

From the three assumptions that have been made and the general equation IV. may be obtained the following equations:

$$s = s_1 - s_2,$$

$$l = l_1 - l_2,$$

$$3 s = c \frac{la^3}{b^3 - a^2},$$

4 
$$s_1 = c \frac{l_1 a_1^3}{b^2 - a_1^2} + s_B,$$

5 
$$s_2 = c \frac{l_2 a_2^3}{b^2 - a_2^3} + s_B$$

where c is a constant. Therefore

$$6 \qquad \qquad \frac{(l_1 - l_2)a^3}{b^3 - a^2} = \frac{l_1a_1^3}{b^2 - a_1^2} - \frac{l_2a_3^3}{b^2 - a_1^2}$$

from which the value of *a* may readily be determined after numerical values have been substituted.

A little consideration will show that a slight change in the radius of a real inner cylinder will have a far greater effect upon that part of its deflection due to its cylindrical surface than it will upon that part due to its ends hence the third assumption is justified for very nearly equal cylinders even though we cannot consider their average radius as being that of the ideal cylinder.

From these dimensions of the ideal cylinder and the other constants of the apparatus the value of K in Eq. V. may be found once for all and thereafter the routine work of the experiment is reduced to the repeated determination of but three or four variables. The following plan was adopted : Method of Observation. - The apparatus was first adjusted :

1. The outer cylinder was set vertically by the leveling screws with the aid of a plumb line.

2. The outer cylinder was centered upon the turn-table until the distance between the point of a wire, held within a millimeter of its surface, and its reflected image did not alter appreciably as it turned.

3. The inner cylinder was put in place and the upper support adjusted until it hung just 5 cm. above the bottom of the outer one.

4. The turn-table was moved horizontally until the inner cylinder centered within a small fraction of a millimeter as measured by a brass gauge.

5. Water, previously brought to its equilibrium temperature, was poured in until it reached a point 5 cm. above the upper surface of the inner cylinder. All bubbles of air clinging to the surfaces were carefully removed.

ó. The mirror attached to the stem was moved into its proper position.

After these adjustments were made (half an hour later):

7. The initial position of the scale image was recorded and the motor started.

8. After a suitable length of time (15 to 45 minutes) the velocity of rotation and the corresponding deflections were observed simultaneously for several minutes.

9. A thermometer was thrust into the water and its temperature noted (this was also done at various other times when opportunity permitted to check any possible change).

The water was then removed by a siphon, the second inner cylinder adjusted in position and the observations repeated. The period of free oscillation of the inner cylinder was occasionally determined between (4) and (5) when it seemed desirable.

The data obtained from a double set of observations taken in this way were averaged together and constitute a single set of values in the final tables.

PRELIMINARY WORK.

Range of Investigation. — The method was first tested roughly for the lowest rates of shear hitherto employed (5 radians per second) and was found to be operative. It then seemed desirable to determine how much lower one might go. Apparently there were no mechanical difficulties in using rates of shear a thousand times lower and the attempt was made.

Two cylinders were constructed for me by Mr. Gaertner similar to those already described except that they had no holes in the end and all but fifty grams of their weight was supported by the water in which they were immersed. A set of quartz fibers was drawn and used for suspensions. A number of trials were made using rates of shear as low as .01 radian per second but it was not found possible with the time and facilities at hand to obtain satisfactory results for rates of shear much below .5 radian per second for two reasons.

I. At lower rates convection currents begin to cause marked irregularities. This is shown by the two curves in Fig. 4. The

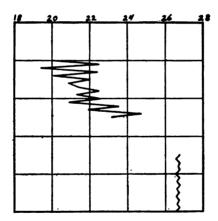


Fig. 4. The upper curve represents the oscillations of the inner cylinder for an interval of fifteen minutes while the apparatus was at rest near a laboratory window and was without thermal insulation. The lower curve represents the oscillations during a similar period under the same conditions save that the outer cylinder was protected by a large water jacket. The inner cylinder was suspended by a quartz fiber suitable for a rate of shear = .05. The ordinates are only roughly proportional to time.

first curve shows the oscillations of the inner cylinder when suspended from a quartz fiber of the proper size for shearing at the rate of .05 radian per second. The observations were taken at night when the apparatus was at rest near a laboratory window and no known disturbing forces were present except convection currents. The second curve represents the oscillations under precisely similar conditions except that the outer cylinder was protected by a large water-bath.

2. A more serious difficulty than the preceding one, which could be greatly minimized by proper thermal insulation, is the length of . time which elapses after the outer cylinder is set in rotation before it exerts its full effect upon the inner one. Fig. 5 represents the position of the inner cylinder for one of the observations in series C(shear = .66) from the time of starting the motor until it had returned

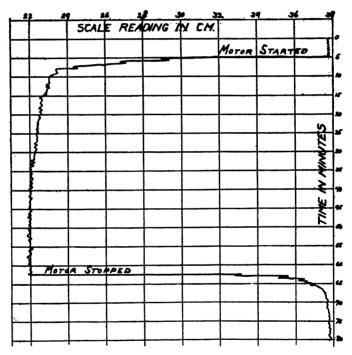


Fig. 5. Curve representing the deflections of the inner cylinder from the time the motor was started until equilibrium had been fully established and until its return to the zero position. This curve corresponds to one of the observations in series C where the rate of shear was about .66 radian per second.

to zero. In this case there was no certainty that the full deflection existed in less than 30 or 35 minutes and to be on the safe side observations were never actually begun before 40 minutes. For rates of shear ten to a hundred times lower than this it might be a matter of hours before equilibrium would exist. For these reasons the lower rates of shear were given up in this investigation at least. The light cylinders and quartz fibers were discarded and three series of observations (Series A, B, C) were undertaken with the apparatus already described using as rates of shear 5.28, 1.29 and .663 radians per second.

Sources of Error. — The principal sources of error may be divided conveniently into three groups: those inherent in the methods of observation, those due to inaccurate adjustments and those arising from changes with time in the physical properties of the apparatus.

*Error Due to Method.* — 1. Angular velocity and deflection: An electric motor was used to drive the apparatus on account of its convenience, but it was not very constant in its speed. Now it appears from what has been said that the deflections of the inner cylinder were some little time in following the changes in angular velocity of the outer one. Hence it was unsafe to assume that the deflection at any given time corresponded strictly with the angular velocity at the moment. It was decided to determine the average speed of the motor for ten minutes or so and from forty or fifty observations of the deflection taken in the same interval to determine its corresponding average value.

To test the reliability of this method the apparatus was set up for the lowest rate of shear (the most unfavorable case) and two sets of values obtained under like conditions for s (deflection) and t(time of one revolution). Now according to Eq. V. the product stof the two quantities should remain constant even if the velocity of rotation changed meanwhile, provided that its average value corresponded each time to the average value of the deflection. Consequently the equality of the two values of st is a test of this correspondence and of the reliability of the method.

Six experiments were performed with the two inner cylinders, using water at different temperatures each time, but maintaining the same conditions during any one experiment except that the speed of the motor changed one or two per cent. These gave the following pairs of values for *st*: long cylinder — (1325.4, 1327.2), (1320.0, 1321.3), (1307.8, 1307.5); short cylinder — (860.2, 863.4), (861.2, 866.9), (838.6, 837.3). It was concluded that the method was L. E. GURNEY.

sufficiently reliable if slightly longer intervals were used with the shorter cylinder.

Errors Due to Inaccurate Adjustments. — The theory supposes among other things that :

2. The cylinders are concentric.

3. The conditions about the ends, i. e., the depth of water and relative position of surfaces, is the same in every case.

To test these points three experiments were carried out. (a) The apparatus was adjusted as well as possible with 5 cm. of water above and below the ends of an inner cylinder, the motor started and after equilibrium had been established readings were taken for s and t. (b) The inner cylinder was displaced about a millimeter from the center — a much greater eccentricity than would occur in practice — and readings were again taken. (c) About I cm. of water was drawn from the top with a pipette. Readings were again taken.

The results of these experiments were as follows :

Experiment.	Av. Defl. s.	Time I Rev. t.	st	
a	17.268	48.73	841.5	
Ь	17.370	48.36	840.0	
c	17.290	48.48	838.2	

It was concluded that no important error might be expected in practice from ill adjustment of cylinders or water levels.

Couette (loc. cit.) has also shown theoretically that in this case, as in others where the magnitude of a physical effect depends upon the relative position of nearly concentric spheres or cylinders (e. g., Air Condensers, Rosa, J. J. Thomson), that a slight eccentricity produces an error relatively much smaller.

Errors Due to Changes in the Physical Properties of the Apparatus. — The chief errors to be looked for in this direction may arise (a) from changes in the elastic properties of the suspensions since

.02 cm.). Its properties were most likely to change and were therefore studied.

4. That its effective length might always remain the same during the frequent interchange of cylinders the ends were soldered into very small brass tubes. These protected ends were clamped into the supports.

5. Its elastic properties changed very slowly with time; the period of free oscillation of the small cylinders about it was 22.675 secs. on April 6 and 22.698 secs. on May 4. Neither did its elastic limit seem to have been reached, for as shown in Fig. 5 it always came back to zero when the motor was stopped.

6. It was feared that its elastic constants might change under the different tensions due to the comparatively heavy cylinders (about 200 gms. and 400 gms.). Accordingly the periods of oscillation of both cylinders were measured when suspended upon it and upon another wire so much larger that it would presumably be unaffected by this difference.

The results gave :

	Period on Small Wire.	Period on Large Wire.
Long Cyl.	27.24	4.653
Short Cyl.	22.70	3.879

This gives  $(27.24)^2/(22.70)^2 = 1.440$  and  $(4.653)^2/(3.879)^2 = 1.439$ . Hence it was concluded that the different weights of the cylinders did not alter the elastic properties of any of the suspensions.

(b) Temperature. -7. As has already been stated there was little reason to fear an appreciable change in the temperature of the water during a single period of observation.

(c) Surface Rigidity. -8. It was found that the surface of the water tended to acquire a rigid condition and that where the stem of the cylinder passed through it, it was capable of exerting a couple that was not only very appreciable but that under certain circumstances might even exceed that due to the whole mass of the fluid below it acting through its viscosity. This effect was most troublesome until discovered. It is considered at greater length in another part of this paper. It was eliminated by allowing a strip of metal, bent into a circle about the stem and fastened to an outside support, to touch the surface of the water. This prevented that

No. 1.]

part of the surface around the stem from acquiring any motion of rotation from the cylinder.

Constants of the Apparatus. -(a) Dimensions of the Real Cylinders. - Their cross-sections were found to be truly circular within 3 or 4 thousandths of a centimeter; the longer inner cylinder was slightly tapering, its average diameter being .007 cm. greater at one end. Their average dimensions as determined by vernier calipers were as follows:

Radius	of the or	iter cy	rlinder	was	5.568 cm. = b
"	" long i	nner	"	"	4.499 cm. $= a_1$
"	" short	"	"	"	4.506 cm. $= a_2$
Length	" long	"	"	"	9.890 cm. $= l_1$
"	" short	"	"	"	$4.957 \text{ cm.} = l_2$

From the value of K in Eq. V. may be obtained by differentiatiou

(7) 
$$\frac{d\eta/\eta}{da/a} = \frac{2b^2}{b^2 - a^2},$$

(8) 
$$\frac{d\eta/\eta}{db/b} = \frac{-2a^2}{b^2 - a^2}.$$

Taking the dimensions of the cylinders from the table given above it appears from these equations that an error of one per cent. in the measurement of  $a_1$  and  $a_2$  would lead to an error of + 5.7 per cent. in the value of  $\eta$ . An error of one per cent. in the measurement of b would lead to an error of - 3.7 per cent. It is thought that the error in the final results arising from the measurements given here is less than that from other parts of the experiment.

(b) Dimensions of the Ideal Cylinder. — Substitution of these values of b,  $a_1$ ,  $a_2$ ,  $l_1$  and  $l_2$  in equations 2 and 6 gives :

Length of ideal cylinder, 4.933 cm. = l, Radius of ideal cylinder, 4.490 cm. = a.

(c) The Quantity M. — The shorter inner cylinder was chosen as the body whose moment of inertia was to be measured.

A cylindrical piece of heavy brass tubing was carefully turned, measured and its moment of inertia calculated. The dimensions of this test piece were

Inner radius = 
$$3.213$$
 cm.  
Outer radius =  $3.489$  cm.  
Mass =  $253.47$  gms.  
: Moment of Inertia =  $2,850$ .

This test piece could be laid upon the cylinder, while it was suspended, in a position concentric with its axis.

The periods of free oscillation of the cylinder without and with the test piece were then determined to be 22.760 secs. and 31.560 secs. Hence it was calculated that

M = 3,089 for the short cylinder.

(d) The Value of K. — From the preceding values obtained for M, b, a and l

$$K = \frac{M(l^2 - a^2)}{4a^2b^2l} = 2.707.$$

All these measurements were afterwards repeated, using another caliper graduated in inches by Brown and Sharpe. When these data were reduced to C.G.S. units and calculated out they gave as a result K = 2.705.

This value of K is constant throughout the investigation but the value of T in Eq. V. must always be obtained by the use of the shorter inner cylinder.

FINAL OBSERVATIONS.

Series A.

Rate of shear = 5.28 radians per second.

Suspension : Steel wire ; length = 19 cm., diameter = .0245 cm. Guard ring not used.

Value of  $\eta = .009319$  at 24° C.

Historically this series was the second to be carried out. It was not found possible to use the guard ring as a protection against surface rigidity, for at this angular velocity eddy currents were set up by it which made the observations irregular and valueless; however, equilibrium was established within ten or fifteen minutes after the apparatus was set in motion and there was little reason to fear surface rigidity effects within this time. Before each of the observations recorded in the following tables the apparatus was readjusted and any possible surface film destroyed by vigorously stirring it with a wire. The water was not renewed each time but only when indicated by dividing lines.

In the tables s refers to the observed scale deflection in centimeters and t is the number of seconds required by the outer cylinder to make one revolution. Observations for each datum were made over an interval of from eight to ten minutes.

In order to combine results each value of st is reduced to a standard condition of temperature and scale distance using as one assumption that the coefficient of temperature change of viscosity is approximately the same at these rates of shear as at ordinary ones; an assumption that seems fairly justified by the data themselves.

The observations are as follows :

t was measured with a stop watch. Its rate was frequently checked by the clock circuit and was found to be very uniform but faster than true time by 2 parts in 1,000. The corrected averages are reduced to true time on this basis.

T was measured by direct reference through electrical contacts

No. of Obs.	<b>s</b> .	t	at	Temp.	st Reduced to $24^{\circ}$ C and to $d = 250$ cm.
1	63.59	6.144	390.7	24.32	402.5
2	63.13	6.188	390.7	.33	402.6
3	62.87	6.200	389.8	.34	401.7
4	63.29	6.169	390.4	24.25	401.6
5	63.18	6.183	390.7	.26	401.9
6	63.39	6.173	391.3	.28	402.7
7	63.14	6.194	391.1	.29	402.6
8	63.01	6.188	389.9	.31	401.6
9	62.70	6.200	388.7	24.42	401.4
10	64.03	6.106	391.0	.43	403.8
11	63.68	6.118	389.6	.44	402.5
12	63.81	6.125	390.9	.45	403.9
13	63.76	6.106	389.3	.46	402.4
		6.161 Av.			402.38 average 401.58 corrected A

Long Inner Cylinder: d (scale distance) = 244.5 cm.



No. of Obs.	\$	t	st	Temp.	st Reduced to $24^{\circ}$ C. and to $d = 250$ cm.
1	45.13	6.303	284.5	24.23	293.9
2	45.02	6.281	282.8	.24	292.2
3	45.17	6.303	284.7	.24	294.2
4	45.02	6.290	283.2	.25	292.7
5	45.23	6.313	285.5	.26	295.2
6	46.46	6.138	285.2	23.99	293.0
7	46.51	6.168	286.8	24.00	294.7
8	46.74	6.129	286.4	.02	294.5
9	47.73	6.019	287.3	.04	295.5
10	47.06	6.036	284.0	24.47	295.1
- 11	47.19	6.027	284.4	.47	295.4
12	47.21	6.013	283.8	.48	294.9
13	46.65	6.106	284.9	24.29	294.7
14	46.48	6.143	285.5	.30	295.5
15	46.45	6.128	284.7	.31	294.6
16	46.99	6.072	285.3	.34	295.5
		6.154 Av.			294.47 average 293.88 corrected Av

Short Inner Cylinder : d (scale distance) = 243.3 cm.

Period of Free Oscillation of Short Cylinder.

Total Time.	No. of Oscillations.	Period.	Average Period 2	
1,163.3	104	11.185		
1,118.2	100	11.182	11.184	

to the clock circuit since greater accuracy is required in these values. Value of  $\eta$ . — From the preceding data we have :

st	for	the	long	inner	cylinder	-	401.58
st	"	"	short	t "	"	=	293.88
st	"	"	ideal	"	""	-	107.70

Therefore

$$\eta = \frac{stK}{dT^2} = \frac{(107.7)(2.706)}{(250)(11.184)^2} = .009319 \text{ at } 24^\circ \text{ C}.$$

Guard ring not used.

Value of  $\eta = .009306$  at 24° C.

This series was carried out in same fashion as the preceding one. The guard ring did not greatly disturb the deflections of the cylinder yet it seemed to do more harm than good and was not used in the final work. It required from twenty minutes to half an hour

No, Obs.		t	st	Temp.	Weight.	st Reduced to $24^{\circ}$ C. and to $d = 250$ cm.
1	21.34	25.20	537.7	24.20	7	555.1
2	21.31	25.04	533.5	.24	8	551.3
3	21.39	25.08	536.4	.25	7	554.4
4	21.45	24.89	533.9	.26	7	552.0
5	21.53	24.96	537.4	.26	9	555.6
6	21.84	24.51	535.3	.28	31	553.6
7	20.88	25.72	537.0	24.04	11	552.3
8	20.87	25.84	539.4	.05	11	554.9
9	21.35	25.10	535.8	.11	31	552.0
10	21.22	25.25	535.8	24.22	13	553.4
11	21.26	25.18	535.3	.23	13	553.0
12	21.42	25.06	536.9	.23	9	554.6
13	21.51	24.92	536.1	.24	13	553.9
14	21.67	24.72	535.6	.25	31	553.6
		25.10 Av.			<b>_</b>	553.38 average.
				1	1	552.28 corrected A

Long Inner Cylinder : d = 243.3 cm.

#### Short Inner Cylinder: d = 244.0 cm.

No. Obs.	\$	t	st	Temp.	Weight.	st Reduced to $24^{\circ}$ C. and to $d = 250$ cm.
1	14.39	24.77	356.5	24.36	31	368.3
2	13.68	26.63	364.3	23.49	13	368.7
3	13.79	26.31	362.9	**	13	367.4
4	13.81	26.31	363.4	**	13	367.8
5	13.86	26.27	364.0		13	368.4
6	13.80	26.25	362.4	••	31	366.8
7	14.73	24.68	363.6	23.60	13	369.0
8	14.82	24.54	363.6	.60	13	369.0
9	14.87	24.45	363.5	.58	13	368.7
10	14.82	24.52	363.4	.57	31	368.6
		25.47 Av.			1	368.15 average.
					1	367.42 corrected A

to establish equilibrium after turning on the motor. Observations were not made in less than thirty minutes after setting the cylinder in motion; the temperature readings were made directly after them. In the other series observations were made over fairly equal intervals; in this one they varied from seven to thirty-one minutes and the results are weighted accordingly in finding averages.

Total Time.	No. of Oscillations.	Period.	Average Period 7
1,231.6	84	14.662	
1,349.0	92	14.663	14.663

Period of Free	Oscillation a	of Short	Cylinder.
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Value of  $\eta$ . — From the preceding data we have :

st	for	the	long	inner	cylinder	-	552.28
st	"	"	short	t "	44	_	367.42
st	"	**	ideal	**	"	_	184.86

Therefore

$$\eta = \frac{stK}{dT^2} = \frac{(184.86)(2.706)}{(250)(14.663)^2} = .009306 \text{ at } 24^\circ \text{ C}.$$

Series C.

Rate of shear = .663 radian per second.

Suspension : Steel wire ; length = 54 cm., diameter = .0200 cm. Guard ring used.

Value of  $\eta = .010013$  at 21° C.

At the angular velocities used in this series considerable time was required to establish equilibrium and observations were never made until forty-five minutes after the motor was started. Surface rigidity made all the earlier work inconsistent. It was eliminated by the use of the guard ring which did not appear to disturb the deflections of the cylin ler as it did for greater velocities of rotation.

The observations were as follows :

Value of  $\eta$ . — From the preceding data we have :

st	for	long	inner	cylinder	=	1,272.9
st	"	short	**	"	=	792.2
st	"	ideal	"	"	=	480.7

No. of Obs.	*	1	st	Temp.	st Reduced to 21°C. and to d=250 cm.
1	24.55	50.32	1,235.4	21.11	1,272.8
2	24.50	50.56	1,238.5	.13	1,276.5
3	24.62	50.04	1,231.8	.15	1,270.3
4	25.54	48.00	1,225.8	21.58	1,277.0
5	25.51	48.00	1,224.7	.59	1,276.1
6	25.48	48.08	1,225.0	.60	1,276.8
7	24.99	49.64	1,240.6	21.07	1,276.8
8	25.02	49.52	1,239.1	.07	1,275.3
9	25.01	49.48	1,237.5	.07	1,273.7
10	25.79	47.48	1,224.6	21.47	1,272.4
11	25.83	47.48	1,226.4	.50	1,275.2
12	25.81	47.48	1,227.4	.53	1,277.2
13	25.86	47.56	1,229.8	.55	1,280.2
		48.74 Av.			1,275.4 average
					1,272.9 corrected Av

Long Inner Cylinder : d = 243.3 cm.

## Short Inner Cylinder: d = 242.7 cm.

No. of Obs.	*	*	st	Temp.	st Reduced to 21° C. and to d=250 cm.
1	16.01	49.12	786.4	20.37	797.8
2	15.97	48.98	782.4	.38	793.9
3	15.99	48.92	782.0	.40	793.9
4	15.62	49.52	773.4	20.66	790.0
5	15.65	49.68	777.5	.69	794.9
6	16.08	48.44	778.9	20.49	792.4
7	15.96	48.64	776.3	.51	790.1
8	15.86	49.28	781.7	.53	796.1
9	15.28	50.43	770.4	20.90	791.7
10	15.38	50.32	773.8	.93	795.7
11	15.19	50.88	772.9	.95	795.2
		49.47 Av.			793.8 average.
					792.2 corrected Av

Period of Free Oscillation	: of	Short	Cylinder.
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Total Time.	Total Time. No. of Oscillations.		Average Period T.
1,116.9	49	22.794	
1,185.4	52	22.796	22.795

Therefore

$$\eta = \frac{stK}{dT^2} = \frac{(480.7)(2.706)}{(250)(22.795)^2} = .010013 \text{ at } 21^\circ \text{C}.$$

DISCUSSION OF RESULTS.

Reliability. — Of the three series I regard B as the most reliable and A as the least. B seems to avoid to a certain extent irregularities peculiar to each of the others.

Oscillation about Zero Position. — None was apparent in A; a slight motion in B; an irregular movement of a millimeter or two in C. These movements were probably due to convection currents.

Oscillation about Deflected Position. -(a) There was a ready response to any change of speed in A; in B and C the response was less ready and probably accounts for some irregularities in the data. The change in deflection was always proportional to the change in speed.

(b) Superposed upon the changes in deflection due to the changes in speed were two others: First—the slight zero oscillations. Second—a rhythmical movement repeated at each revolution of the outer cylinder. This movement was 3 or 4 millimeters (scale deflection at 2.5 meters) in A; a millimeter or so in B and was not observed in C. The explanation would seem to be that the cylinders were not perfectly circular in cross-section and there was consequently a bodily motion of the entire fluid corresponding in period to the period of rotation. The effect was relatively slight even in A. In A and B the average position of each movement was recorded during the observation interval and thus the number of recorded positions gave also the number of revolutions in the interval.

Conclusion. — The values of  $\eta$  found in A, B and C are .8 per cent., .7 per cent. and .9 per cent. higher than those given by Landolt and Börnstein. Any departure from a truly circular cross-section in the cylinders or any tilting or lack of concentricity would cause an apparent increase in  $\eta$ , since the ideal case is the case of minimum deflection. The rhythmical movement in A and the measurements of the cylinders show a slight departure from a perfect cross-section. The actual case may also differ slightly from the ideal in other ways, and the tendency would usually be to increase the apparent value of  $\eta$ . For these reasons I do not feel that these results justify the claim that the viscosity of water is greater at these low rates of shear. But I feel that they justify the counter-claim that it is not more than one per cent. greater, if at all.



## SOME OBSERVATIONS ON THE SURFACE RIGIDITY OF WATER.

#### BY L. E. GURNEY.

I was observed during the earlier part of the writer's work on the viscosity of water at low rates of shear that it apparently increased if the water was allowed to stand for some time in the cylinder. It was thought, at first, that the water might have absorbed air or that its contact with metal might have had such an effect, but deflections were afterwards obtained so great as to make this out of the question. The cause of the effect was for a long time unknown until the writer chanced one day to stand in the path of a ray of light reflected from the surface of the water and noticed that the dust particles upon it started into motion as if it were a rigid plate when the motor was turned on.

Where the stem of the inner cylinder passed down through the surface a bit of wire was wound about it with a free end pointing downward to indicate the proper water level; this point of the marker was about one centimeter from the stem. Further investigation showed that if the water had been standing for a considerable length of time and if the surface touched the point of the wire that, acting on this single point of application and on this short couple arm, it could exert a couple even greater than that which the whole mass of the fluid below it exerted upon the cylinder by virtue of its viscosity.

No special study was made of this phenomenon, since time did not permit; the effect was eliminated by allowing a guard ring to touch the surface of the water about the stem, thus keeping it at rest. Yet certain incidental observations may be of interest; these were all made while the apparatus was adjusted for the lowest rate of shear.

## Magnitude of the Effect.

1. The couple exerted upon the point of wire and stem was much greater than that exerted upon the stem alone.

2. The deflection produced by the surface couple was in some instances greater than due to the viscosity of the water. In one case when water, originally taken from the bottom of a nearly empty carboy, had remained in the cylinder undisturbed for four days, the surface effect was at least four or five times greater than the viscosity effect.

#### Resistance to Stress.

3. On one occasion, when the water had stood for a day or twothe outer cylinder was slowly turned through an angle of about I degree. The inner cylinder was deflected about .3 of a degree and *remained* in this position without returning to zero. The outer cylinder was then turned through another degree; the inner cylinder followed to .6 of a degree and remained fixed for a considerable time, coming to zero only after an hour or more.

#### Development of Rigid Surface.

4. The water surfaces became noticeably rigid in a few hours or a few days, depending upon the previous history of the fluid.

5. Vigorous stirring destroyed the rigidity of the surface.

6. In a general way the water which held the most air in solution seemed to develop a rigid surface most quickly. The reasons for this opinion are that:

(a) Water taken from the bottom of nearly empty carboys and long exposed to air most readily developed such a surface.

(b) Water freed from air by boiling was noticeably slower in assuming this condition.

(c) Water which readily assumed this condition oxidized the metal of the cylinders which were not attacked by fresh air-free water.

I could not judge whether the dissolved air stood in a causal or incidental relation to the effect; neither did I observe that change of temperature or rate of evaporation influenced its formation, but the conditions were not well suited to observations of this character.

The last observations may indicate, however, that the formation

No. I.]

#### THE VISCOSITY OF WATER.

## EFFECTS OF THE SOLUBLE CONSTITUENTS OF GLASS UPON THE VISCOSITY OF WATER AT VERY LOW RATES OF SHEAR.

#### BY L. E. GURNEY.

IN the *Philosophical Magazine* for May, 1905, Professor A. W. Duff gives an account of certain experiments upon the viscosity of water at low rates of shear — about five radians per sec. The method of flow through horizontal glass tubes under very small pressures was used. Values were obtained for the coefficient that were in some instances nine or ten per cent. higher than those found by the ordinary methods. After varying the experiment in a number of ways to find the explanation of this increased value for the coefficient Professor Duff arrived at the conclusion that "Very minute quantities of the constituents of glass dissolved out by water have very large effects on the viscosity of water at low rates of shear."

Two experiments were performed to test this conclusion using the apparatus and methods described in the preceding paper.

### Experiment 1.

About a square foot of window glass was carefully cleaned, laid between pads of filter paper and crushed into a coarse powder with a hammer. The powdered glass was then put into a litre bottle of distilled water and allowed to stand for a week. It was then filtered off into the outer cylinder, the apparatus adjusted, set in motion and the deflection observed for the smaller inner cylinder. The glass solution was then replaced as quickly as possible by freshly distilled water and the deflection observed under similar conditions. The following observations are averages for intervals

In the last column the two valves of *st* are reduced to the same temperature and scale distance.

#### Experiment 2.

Five or six feet of soft german sodium-glass tubing of the sort described by Professor Duff was crushed between filter paper, put in a mortar and reduced to a fine powder. This was soaked in a litre bottle of distilled water for a week, the bottle being occasionally shaken up, and the viscosity of the solution compared as before with that of pure water by noting the deflections of the small inner cylinder when immersed in them under similar conditions. This experiment also differs from the preceding one in that a guard ring was used to eliminate possible surface effects and that several sets of observations were taken. The rate of shear as before was about .66 radian per sec.

	8	t	st	Temp.	
Glass Solution.	14.90	49.10	731.8	23.05	Average value of
	14.91	48.91	729.3	**	st reduced =
	14.94	49.98	731.3	• •	787.9.
	14.85	49.10	729.3	**	
Pure Water.	14.86	48.65	722.9	23.32	Average value of
1	14.77	49.05	724.4	**	st reduced ==
	14.78	48.98	723.7		784.5.
	14.71	48.98	721.0		
	14.86	48.60	722.0		'i •

*Conclusion.* — In these experiments whose parts were carried out under precisely similar conditions, no differences between the viscosities of glass solutions (which must have been far stronger than those used by Professor Duff) and those of pure water were found that could not be accounted for by observational errors. The results do not, therefore, appear to sustain the contention that the viscosity of water is noticeably increased at low rates of shear by minute quantities of the soluble constituents of glass.

#### THE STABILITY OF WESTON CELLS.<sup>1</sup>

BY HENRY S. CARHART.

E VIDENCE has recently been adduced by Professor Hulett<sup>2</sup> tending to the conclusion that the chemical stability of the Weston or cadmium cell is inferior to that of the Clark; that its electromotive force slowly declines to an extent that renders it less suitable for a primary standard than the Clark cell; and that this loss of electromotive force is probably due to some secondary reaction at the surface of the mercury constituting the positive electrode.

This paper is a contribution to this subject derived from a study of a series of cadmium cells set up nearly five years ago and all save one still in good order. They were made by myself before the work began in conjunction with Professor Hulett, which was reported on by us before the American Electrochemical Society.<sup>3</sup> They consist of the series  $B_1$  to  $B_{10}$ , including the  $B_7$ , which has been for four years my standard of reference, and they were set up at the dates indicated in the following table :

 Cell.
 Date.
 Mercurous Sulphate.

  $B_1$  January 18, 1903.
 Merck's, washed with water.

  $B_2$  March 9, 1903.
 March 9, 1903.

  $B_4$  March 9, 1903.
 Precipitated with  $H_2SO_4$  from a hot solution of  $HgNO_3$ .

  $B_4$  June 22, 1903.
 Precipitated with  $H_2SO_4$  from a hot solution of  $HgNO_3$ .

  $B_6$  June 22, 1903.
 Precipitated with  $H_2SO_4$  from a hot solution of  $HgNO_3$ .

  $B_9$  June 22, 1903.
 Precipitated with  $H_2SO_4$  from a hot solution of  $HgNO_3$ .

Cells  $B_2$  to  $B_5$  were set up with a cadmium sulphate solution which had been neutralized with cadmium carbonate and the excess

<sup>1</sup>Contribution from a reseach made with the aid of a grant from the Elizabeth Thompson Science Fund.

<sup>3</sup> Transactions, Vol. V., 1904, p. 59, and Vol. VI., 1904, p. 109.

<sup>&</sup>lt;sup>3</sup> PHYS. REV., Vol. XXV., July, 1907.

removed (supposedly) by treatment with washed mercurous sulphate. This was the old method often used to neutralize a zinc sulphate solution. But there was evidence later that the solution of cadmium sulphate was in reality somewhat basic. Hence for a long period these four cells had a lower electromotive force than the others of this group. They now have practically identical values with the others.

The following table of comparisons shows how these cells have maintained their relative values :

Cell.	July, 1903.	Septem- ber, 1903.	February, 1904.	July, 1905.	July, 1906.	March, 1907.	October, 1907.
<i>B</i> .	1.01922	1.01934	1.01936	1.01937	1.01940	1.01939	1.01940
$B_1$ $B_1$	20	25	28				34
<b>B1</b>	22	28	30	1			36
B <sub>4</sub>	19	25	28		1		35
B	20	27	30				35
B	36	35	35	1.01935	1.01935	1.01935	37
B,	36	36	36	36	36	36	36
$B_8$	37	36	35	34	35	35	37
<b>B</b> ,	36	34	33	33	33	34	36
<i>B</i> <sub>10</sub>	36	35	35	36	37	37	
	M	ans,		1.01935	1.01936	1.01936	1.01936

These cells have been kept continuously in a bath controlled by a thermostat since December, 1903, and very nearly at 21.1° C. All comparisons have been made at this temperature. Cells  $B_3$  to  $B_5$  it will be seen have gradually approached the others in value. Hence the mean of the whole group has slowly risen a trifle. The mean of the last five has remained 1.01935 or 1.01936 for the past four years.

The materials for the first five cells were not prepared with much skill. The mercurous sulphate for all except  $B_1$  was made by dissolving mercurous nitrate, purchased as pure, in water acidified

amalgam and for the positive electrode. The amalgam was prepared by weighing out the requisite amounts of mercury and cadmium and heating them together over a water bath.

All these cells are of the *H*-form and they were hermetically sealed in the manner described in the papers already alluded to in the Transactions of the American Electrochemical Society.  $B_1$  was the first cell sealed in this manner. It is still in good condition.

Cells set up with mercurous sulphate prepared either electrolytically,<sup>1</sup> or by precipitation in accordance with the preliminary specification of the National Physical Laboratory in London, have an electromotive force twenty parts in 100,000 lower than this *B*group. The *B*-cells are higher than those made at the Bureau of Standards in Washington by the same amount.

What evidence now is at hand touching the question of the permanence and stability of this *B*-group of cells? Have they declined in the four years during which they have been under observation? The comparisons made from time to time have been directed toward the question of relative values among themselves, and to the study of cells made up with the object of determining the effect of varying the method of preparing the materials in some particular. But occasional comparisons have been made with Clark cells in which the mercurous sulphate was prepared electrolytically. These occasional comparisons serve to evaluate the Clark at 15° in comparison with the cadmium at 20°, the temperature reductions being made by means of the formulæ of the Reichsanstalt:

Clark,  $E_t = E_{15} - 0.00119(t - 15) - 0.000007(t - 15)^2$ . Cadmium,  $E_t = E_{20} - 0.000038(t - 20) - 0.0000065(t - 20)^2$ .

The comparison is in each case with  $B_{\gamma}$ , the value of which relative to the others from  $B_6$  up has remained constant.

	April 18, 1904.	Nov. 25, 1904.	June 24, 1907.	Oct. 30, 1907.	Dec 7, 1907.
<i>B</i> <sub>7</sub>	1.01940	1.01940	1.01940	1.01940	1.01940
$H_{1} - H_{10}$	1.43382	1.43383			•
Clala		:	1.43382	1.43382	
$Cl_{11}, Cl_{12}$		,			1.43382

The group of *H*-cells were set up with electrolytic mercurous sulphate washed with dilute sulphuric acid and finally with zinc <sup>1</sup>Trans. Amer. Electrochem. Soc., Vol. VI., 1904, p. 109.

sulphate solution. Cell  $Cl_{31a}$  is one sent to me from the Bureau of Standards in Washington. Cells  $Cl_{11}$  and  $Cl_{12}$  were set up November 8, 1907, with mercurous sulphate precipitated by the method recommended by the National Physical Laboratory.

Unfortunately I have no comparison on record in 1903 which enables me to evaluate a Clark directly by means of the *B*-cells at that time. But the above comparisons, extending over a period of more than three and a half years, show undeniably that the *B*-cells have maintained their electromotive force. The only alternative supposition is that the Clarks have lost by precisely the same per cent. But this is inadmissible, since the Clarks have been set up at different times and have not had the same test of aging as the *B*-cells.

It will be noticed that the Clarks are eighteen parts in 100,000 below 1.434 at 15° C. The value 1.01940 for the cadmium cell at 20° C. was obtained from 1.434 by dividing by the ratio  $\frac{\text{Clark at } 15^{\circ}}{\text{Cadmium at } 20^{\circ}} = 1.4067$  as the mean of several series of comparisons made at the Reichsanstalt. It now appears that this *B*-group of cadmium cells have a slightly higher electromotive force than those now made by accepted methods. If then they are rated too low, the Clarks will also be too low. If they had fallen off in electromotive force and so were rated too high, the Clarks would also come out too high.

Whatever then may be the fact as to a lack of stability in the case of cadmium cells made with electrolytically prepared mercurous sulphate, these old cells made with precipitated mercurous sulphate meet every requirement of permanency. They are fully the equal of the Clark cell in this regard, and are decidedly superior when considered from the point of view of the permanency of the containing glass cell. The Clarks almost invariably crack at the negative electrode by the alloying of the platinum wire in contact with the zinc amalgam. No such difficulty is encountered with platinum and cadmium amalgam. It is very difficult to make and seal glass cells with a platinum wire sealed into the glass in so perfect a man-

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## THE

# PHYSICAL REVIEW.

## THE DISCHARGE OF ELECTRICITY FROM POINTED CONDUCTORS.

#### BY JOHN ZELENY.

I. In a previous paper <sup>1</sup> are given the results of some experiments on the discharge of electricity from a set of points which consisted of cylindrical wires of different diameters whose ends were either hemispherical or plane. The points were placed opposite a brass disc and were enclosed in a cylindrical vessel containing dry air.

It was found that the discharge from points of this character gives consistent results which can be readily reproduced, and the way that the discharge depends upon the diameter of the point was given special consideration.

The apparatus, which is fully described in the paper mentioned, has been used for studying the discharge from steel needle points of various degrees of sharpness and from brass conical points of various sizes, and the results are here recorded together with those of some other experiments on point discharge.

The subject-matter is considered under the following subdivisions :

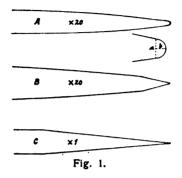
(a)	Positive discharge from steel needle points	११ 2, 3
(6)	Relation between current, voltage, minimum potential, and diameter	r of points § 4
(r)	Negative discharge from steel needle points	§ 5
(d)	Formation of oxides on steel points	\$6
(e)	Positive discharge from 12° conical points	88 7, 8
(f)	Negative discharge from 12° conical points	29
(g)	Discharge to different parts of a spherical surface	§§ 10, 11
(1)	Discharge at different pressures	§§ 12, 13
(i)	General remarks	§ 14
	Summary	

<sup>1</sup> J. Zeleny, PHYS. REV., 25, p. 305, 1907.

#### JOHN ZELENY.

## POSITIVE DISCHARGE FROM STEEL NEEDLE POINTS.

2. The steel needle points used were prepared from ordinary sewing needles, a variety of sizes of the points being obtained by altering the ends of some of the needles on an oil stone.



Two kinds of commercial needles were met with. In the one (see A, Fig. 1) the angle between the opposite walls of the needle increases gradually as the point is approached, reaching a value of from 10° to 12° at the point itself. In the other kind (see B, Fig. 1) there is a sudden increase in the taper near the end of the needle, the angle changing at a

distance of about one half a millimeter to a millimeter from the end, from about  $10^{\circ}$  to over  $20^{\circ}$  and to as much as  $30^{\circ}$  in one make. The sharpest points are found on needles of this type. Usually the finest needles were found to be of the first type and the coarser ones of the second type but in an assorted package from one maker the needles of all sizes were of the second type.

The sharpness or size of the needle point will be designated in each case by giving the diameter of the cross-section of the needle at a place where this diameter (a, Fig. I) is twice the distance (b,Fig. 1) of this cross-section from the tip of the needle. The measurements were made with the stage micrometer of a microscope, the location of the cross-section specified being estimated by eye alone.

In order to describe more exactly the general nature of the needles used, not only is this diameter of the point stated for each needle but its length and maximum diameter are also given, together with the angle of the average taper for the first two or three point-diameters from the end. It has been found that one of the chief differences between different needles as regards point discharge lies in the value of the taper at the end. The angle of this taper usually increases as the points get sharper, because it is both difficult and inadvisable to make very sharp points with this angle small.

Preliminary experiments made in the open air with a promiscuous lot of needles gave results which varied quite regularly with the diameter of the points, but among the finest points one would be found now and then with the taper exceptionally obtuse, which would give results considerably different from the rest. The largest difference observed was one of seven per cent., in the voltage required to produce a given current.

The experiments here described were carried out in exactly the same way as those described in the paper already referred to. The needles were supported above the plate by means of a brass rod, in the end of which a slot was provided for holding them axially.

3. The results obtained for the positive discharge in dry air with a number of selected needles placed at a distance of 1.5 cm. from the plate, are given in Table I. The temperature was practically 19° C. and the air pressure 74.7 cm. throughout the whole series of experiments.

Point Number.	1	2	3	4	5	6
Diameter of Point in Mm.	.0068	,013	.055	. <b>096</b>	.198	.364
Length of Needle in Mm.	34.7	x	39-7	36.3	49.0	45-5
Max. Diameter of Needle in Mm.	.51	x	.82	•57	1.17	1.03
Taper of Point.	2 <b>6</b> 0	x	24 <sup>0</sup>	120	9°.3	7°•3
Starting Potential.	2,650	2,700	2,900	3,025	3,550	4.375
	3,000	3,000	3,500	3,500	4,000	4,500
<b>b</b> 0	2.8	2.3	5.7	4.5	5.9	2.3
ling	4,000	3,500	4,000	4,000	5,000	5,000
ouo .	13.6	6.8	11.9	10.7	19.2	9.6
res	5,000	4,000	5,000	5,000	6,000	6,000
correspo	28.3	13.6	26.6	26.0	40.1	28.8
	6,000	5,000	6,000	6,000	7,000	7,000
s with 10-1	50.9	28.8	49.2	47.5	64.4	50.9
110	7,000	6,000	7,000	7,000	8,000	8,000
volt s in	73.5	50.3	73.5	73.4	92.71	79.1
en n	8,000	7,000	8,000	<b>8,000</b>	9,000	9,000
ials in v currents	104.5 <sup>1</sup>	76.3	101.7	102.3	131.1'	117.0
Potentials in volts with corresponding currents in 10 <sup>-1</sup> amperes.		8,000 i	8,350	9,000		9,500
ote		104.5	118.1	141.2	1	141.3
Ë4		8,500				
1		125.4		i	1	

T.	A B	L	E.	I	
		_	_		٩

Positive Discharge from Steel Needle Points. Distance from Plate = 1.5 Cm.

<sup>1</sup>Current more or less intermittent as indicated by telephone.

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The results have been reduced to a pressure of 74 cm. and a temperature of  $22^{\circ}$  C. to make them correspond to the conditions prevailing in the experiments described in the previous paper. The way in which this reduction is made is explained in §§ 20 and 21 of

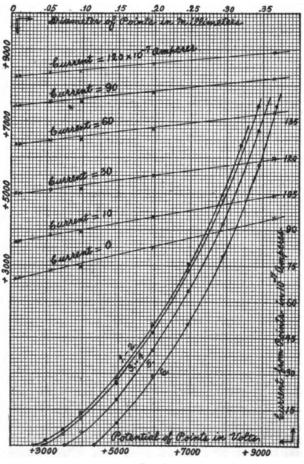


Fig. 2.

points no. 1 and no. 2, and for the points no. 3 and no. 4 are so close together that but one curve is drawn for each of the two cases.

The curves in the upper part of the figure were drawn to show whether there is any relation between the size of the points and the voltage necessary to produce a given current. The potentials taken from the potential-current curves were plotted against the size of the points for each of the currents given. It is seen that there is good regularity in the results and that in each case the potential increases linearly with the size of the point. In view of this regularity, it is now possible to construct from these curves a potentialcurrent curve for a needle point of any size, provided however that the angle of the taper at its point approximates to that on those needles here used which are of about the same point diameter.

The fact that the voltage required to produce any current increases linearly with the diameter of the point is incidental to the way that the angle of the taper increases as the points diminish in diameter. Had the taper of the finest points been as small as that of the larger ones their potentials for the same current would have been smaller than they are.

## Relation Between Current, Voltage, Minimum Potential, and Diameter of Points.

4. The relation between the current and voltage for any one point is fairly well represented by Warburg's formula, C = aV(V - M), where V is the voltage of the point, M the minimum voltage required to start a current, and a constant whose value depends upon the point used. This constant was found to increase linearly with the diameter of the point, so that it is possible to represent the results for all of the points by one formula, the current in amperes being given by,

$$C = 2.58 \times 10^{-13} (1 + .319d) V(V - M),$$

where d is the diameter of the point in millimeters.

In Table II., a comparison is made of the values of the current obtained for several potentials, by the use of this formula and the observed values as taken from potential-current curves similar to but larger than those in Fig. 2.

### TABLE II.

Comparison of Observed Currents with those	Calculated by the Formula, $C=2.58 \times 10^{-13}$
(1 + .319d)	V(V-M).

Dia	.0068	.012 2,665	.°55 2,860	.096 2,985	.198 3,505	.364 4,320	
	2,615						
Voltage.		1	I				
3,000	Current calc.	3.0	2.8				
	observ.	3.0	2.6				1
4,000	Current calc.	14.3	13.8	12.0	10.8	5.4	
	observ.	14.3	14.0	12.1	11.3	5.7	
5,000	Current calc.	30.9	30.2	28.0	26.7	20.5	9.8
-	observ.	30.2	30.2	28.0	27.3	20.2	10.3
6,000	Current calc.	52.6	51.9	49.4	48.0	41.1	27.3
	observ.	52.0	52.0	49.7	48.6	40.6	29.0
7,000	Current calc.	79.4	78.7	75.9	74.6	67.2	54.0
	observ.	79.3	79.3	76.6	75.3	66.7	53.2
8,000	Current calc.	111.6	110.9	107.8	106.6	98.6	84.8
	observ.	112.3	112.3	108.2	107.6	100.0	83.2
9,000	Current calc.			144.7	144.0	135.8	121.3
	observ.	I		143.4	143.4	136.5	122.4

It is seen that the two sets of values are in good agreement.

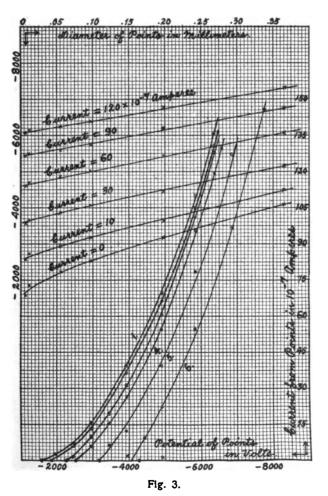
Since the minimum potential required to start a current increases linearly with the diameter of the point, as is shown by the potentialdiameter curve for C = 0 in Fig. 2, its value in volts can be represented by the relation, M = 2,590 + 4,750d, where d is again the diameter of the point in millimeters.

NEGATIVE DISCHARGE FROM STEEL NEEDLE POINTS.

5. The results which were obtained for the negative discharge in dry air from the same set of needle points as used above, are given in Table III. The distance of the points from the plane was again 1.5 cm. The temperature throughout the readings was nearly constant at  $19^{\circ}$  C. and the air pressure was 74.7 cm. The starting potential was determined first in each case and then the currents were obtained for gradually increasing voltages. Where readings were repeated the average value is given.

The results, reduced to a pressure of 74 cm. and a temperature of  $22^{\circ}$  C., are represented graphically by the lower right-hand curves in Fig. 3. The points agree quite well with their respective

curves. Nevertheless, the smaller negative currents often show considerable irregularity. This is especially the case after a point has been used with the higher currents, as some resistance to the flow of small currents seems to be introduced



thereby on the surface of the point, so that the values now obtained with a given voltage are much below the normal values

## TABLE III.

Negative Discharge from Steel Needle Points. Distance from Plate = 1.5 Cm.

Point Number. Diameter of Point in Mm. Starting Potential.			I	2 .012 1,900	3 .055 2,250	4 .096 2,550	5 .198 3,225	6 .364 4,350
		m.	.0068 1,600					
	2,000	ti ti	2.8					
	2,500	amperes		7.3	3.0			
	3,000		16.0	14.3	10.1	5.9		
points.					19.6	15.7	6.2	
io	4,000	3	39.2	36.4	31.4	26.9	12.3 <sup>1</sup>	•
i jo	4,500	s						9.5
	5,000	ă	69.4	66.1	60.5	54.3	<b>39</b> .2 <sup>1</sup>	22.4
Potential	6,000	8	109.8	104.7	101.4	95.2	78.4	54.9 <sup>1</sup>
ote	6,500		135.5	130.6	127.7	119.3		
<b>P</b> 4	6,700					129.9		
	7,000						127.2	96.9
	7,925	5						145.6

currents it may apply. As the voltage is increased when these abnormal conditions obtain, the resistance mentioned disappears more or less suddenly and the current rises to its normal value.

The curves in the upper part of Fig. 3 show the relation between the size of the points and the voltage required to produce the current given in each case. These curves can be used as before for the construction of a potential-current curve for a point of any intermediate diameter, when this has a taper corresponding to that of the points here used. The results for one of the points nos. I and 2 do not agree well with the rest, and there is reason to believe that the discharge from no. 2 was retarded for some reason.

The relation between the current, voltage and the diameter of the points is not as regular in this case as it was for the positive discharge but is given approximately by the formula,

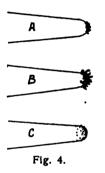
 $C = 4.18 \times 10^{-13} (1 + .63d) V(V - M),$ 

where the letters have the same significance as before.

FORMATION OF OXIDES ON STEEL POINTS.

of the point. This is especially true if the point has been discharging positive electricity. The difference between the positive and the negative discharges in this respect is very marked.

As an example of this action A, in Fig. 4, shows the appearance under the microscope, of the end of a steel needle point after a positive current of about 10<sup>-5</sup> amperes had been flowing from it for five minutes. The substance on the end of the point is of a reddish



brown color, and is doubtless an oxide of iron since it does not form on a platinum point. B, Fig. 4, shows the same point after the same current had been flowing from it for 44 minutes. It is noticed that the material is attached to the point in irregular pieces which extend outward some little distance. The substance is readily removed with a cloth leaving the surface of the point apparently as bright as ever. It is natural that the presence of this material should have

some effect upon the discharge current, and points which have been used for some time must be cleaned to have them regain their normal condition.

When the same point was used with a negative current of the same value for five minutes, it showed no change in appearance. Gradually, however, a readily removable tarnish appeared on the point for a distance of a little over its diameter, dulling somewhat the bright luster of that portion of the needle. The appearance seemed to indicate an accumulation of a lot of fine dark particles. After the negative current had been flowing for over an hour, the point had the appearance shown by C in Fig. 4. The little patch at the very end of the point was of the same reddish-brown color as the accumulation in the case of the positive discharge, but it was in the form of a thin coating. The rest of the deposit was black and some of the larger particles showed a black luster as if they were coal dust.

The reason why the oxide forms so much more readily during

of the iron oxide molecules they unite more readily with the iron than do the positive ions which are carried to the metal surface during the negative discharge.

The deposit can hardly be due to the ozone which is formed by the discharge, attacking the iron, as the ozone is formed in not very unequal quantities during both the positive and negative discharges.

POSITIVE DISCHARGE FROM 12° CONICAL POINTS.

7. Since the taper at the ends of steel needles varies so much for the different needles and of necessity changes along the length of the needle, it was thought worth while to study the discharge from a number of points where this angle is the same for all and remains unchanged for some distance back from the point. Six brass conical points were therefore made, the angle of whose cones was  $12^{\circ}$  for all alike. These cones were 6.35 mm. in diameter at the base (see *C*, Fig. 1), and tapered uniformly to the points which were rounded off so as to be of different diameters. The diameters were measured in the same way as was done with the steel needles.

Point Number.		Point Number. I		2	3	4	5	6
Diameter of Point in Mm.		.060	.107	.336	.464	.64	1.09	
81	tarting Potent	tial.	2,825	3,125	4,500	5,000	5,850	7,525
	3,000		1.7		l	l		
	3,500		6.2	3.9				
	4,000	S.	12.3	9.0		1		
	4,500	per	19.2	15.1			1	
lts.	5,000	amperes.	27.4	23.5	6.2			
20	5,500	5	38.1	33.4	14.6	7.8	1	
.9	6,000	10-1	48.1	43.1	22.9	15.7	3.3	
points in volts.	6,500		59.9	54.8	32.8	25.2	11.8	
D	7,000	nts	72.2	66.6	43.7	35.3	21.3	
	7,500	.io	83.9	78.4	54.8	45.4	30.2	
a	8,000	8	98.5	94.0	67.7	59.3	42.5	10.0
enti	8,500	fro	117.7	112.51	85.0	75.0	58.1	24.1
Potential of	9,000	at .	136.6 <sup>1</sup>	132.0 <sup>1</sup>	103.0	92.9	75.0	39.2
-	9,500	Current from points in			124.1 <sup>1</sup>	114.0 <sup>1</sup>	95.1	57.3
	9,725	บี			132.5 <sup>1</sup>	,		
	9,825					128.8 <sup>1</sup>		
	10,000						115.2	76.

TABLE IV.

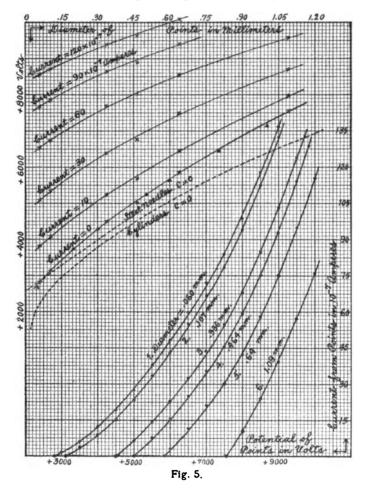
Positive Discharge from 12° Conical Points.

<sup>1</sup>Currents marked with a figure (<sup>1</sup>) were somewhat intermittent.

THE DISCHARGE FROM POINTS.

The results obtained for the positive discharge in dry air from these points when placed at a distance of 1.5 cm. from the plate in the same apparatus as used before, are given in Table IV.

The temperature during the experiments was practically constant



at  $21^{\circ}$  C., and the pressure was 73.7 cm. To reduce the results to a temperature of  $22^{\circ}$  C. and a pressure of 74 cm. as has been done in the other cases would only require a correction of the order of one tenth of one per cent.

The results are represented graphically by the curves in the lower right hand portion of Fig. 5.

No. 2.]

The individual readings are seen to be in good agreement with their respective curves. In the upper part of the figure are shown the potential-diameter curves for the various currents given, the points for each current being taken from the potential-current curves in the lower part of the figure. The good agreement of these points with their respective curves shows the regularity in the results, the values from any point being dependent upon the size of the point only, and not upon any peculiarities of its surface.

8. The relation between the current and potential may be represented again fairly well for each point by the formula, C = aV(V - M), although at the highest voltages used the observed values tend to be larger than what this formula demands. The values of *a* obtained for the smallest points are nearly alike, but they increase rapidly for the larger points, so that the current in amperes from any point may be approximately represented by the formula,

$$C = 2.49 \times 10^{-13} (1 + .176d^3) V(V - M),$$

where d is the diameter of the point in millimeters. In the cases previously considered d appeared in the first power.

#### TABLE V.

Comparison of Observed Currents with those Calculated by the Formula,
$C = 2.49 \times 10^{-18} (1 + .176d^3) V (V - M).$

Diamete	Diameter of Point in Mm.		.107	.336	.464	.64	1.09
	2,825	3,125	4,500	5,000	5,850	7,525	
Voltage.							
4,000	Current calc.	11.7	8.7				
	observ.	12.2	8.9				
5,000	Current calc.	26.8	23.4	6.3	1		
	observ.	27.9	23.7	6.2			
6,000	Current calc.	47.4	43.0	22.6	15.2	2.4	
	obseiv.	48.0	43.0	22.7	15.3	2.8	
7,000	Current calc.	72.6	67.4	43.8	36.0	21.0	
	observ.	71.0	66.0	42.4	34.5	20.0	
8,000	Current calc.	101.5	97.1	70.1	60.8	44.7	11.6
	observ.	100.3	94.1	68.5	59.6	43.0	10.6
9,000	Current calc.	138.2	130.7	101.6	91.2	73.9	40.6
	observ.	136.6	132.0	103.0	93.0	75.0	40.0
10,000	Current calc.					108.1	75.6
	observ.					115.0	76.0

The degree of agreement between the values obtained from this formula and the experimental values taken from the potential-current curves in Fig. 5, is shown for several potentials by the comparison given in Table V.

The potential required to start a current increases with the diameter of the point, in a more complex manner than it did in the cases given before, but its value may be obtained quite accurately for any point by means of the formula,

$$M = 1,980 + 5,200d^{-1}$$

where d is again the diameter of the point in millimeters.

Some values obtained from this formula have been plotted as triangles on the curve for C = 0 in Fig. 5, and the good agreement of these points with the observed values is to be noted.

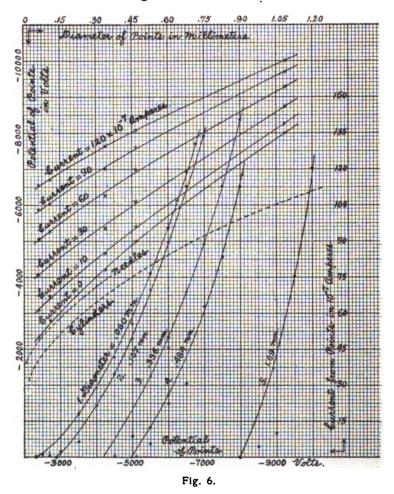
One of the main physical differences between steel needles and these conical points is that at some distance back from the point the needles approximate to cylinders while in the cones, of course, no such change takes place. The difference in the formulæ necessary to represent the results in the two cases is probably due to this difference.

# NEGATIVE DISCHARGE FROM 12° CONICAL POINTS.

9. The results obtained for the negative discharge in dry air from the same conical points as used above when placed at a distance of 1.5 cm. from the plate, are given in Table VI. The temperature throughout was approximately 18°.2 C. and the pressure 72.2 cm.

The results, for the larger points especially, are quite irregular. With the point .64 mm. in diameter the current fluctuated so much that it was not possible to take any readings at all. A star is placed opposite the values of those currents which are given where the telephone indicated an intermittence. The values for the smallest currents were erratic and fluctuated somewhat. Some irregular resistance to the discharge seemed to be present on the surface of the point which only disappeared after the current had reached a certain value.

The results are shown graphically in the lower part of Fig. 6. In drawing the curves some of the erratic values for the smaller currents were disregarded altogether. The results are not regular enough, as a whole, to permit of being used to test any formula, but Warburg's formula appears to hold well for the smallest points, the value of the constant for point no. I being 4.3, in the same units as have been used throughout.



The curves in the upper part of Fig. 6 again give the relation

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# No. 2.] THE DISCHARGE FROM POINTS.

current curves without regard to the low erratic values of the current which so often appeared.

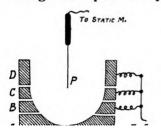
DISCHARGE TO DIFFERENT PARTS OF A SPHERICAL SURFACE.

# TABLE VI.

Point Number.		I	2	3	4	5	
Diameter of Point in Mm.		.060	.107	.336	.464	1.09	
Sta	arting Potent	ial.	2,300	2,875	4,500?	5,100	8,000
	2,500		1.2				
	3,000		3.9	2.0	1		
	3,500	ŝ	18.0	6.2			
	4,000	Der	28.7	21.7			
points in volts.	4,500	amperes.	41.4	34.7			
DA I	5,000	1	55.4	49.5	8.9*	1.1.1.1	
s in	5,500	10	76.5	69.2	33.8	12.5*	
int	6,000	в.	95.6	89.5	50.0	26.0*	
od	6,500	Current from points in	118.8	113.0	68.7	30.4*	
Jo	6,750	io	130.5				
lal	7,000	E		133.9	89.0	63.0	
Potential of	7,500	fro			112.6	83.3*	
Pot	8,000	nt			140.8	112.6	
	8,500	Inte			1		4.5*
	9,000	ů					10.1*
	9,500						75.5*
	10,000						120.5*

Negative Discharge from 12° Conical Points.

10. Warburg<sup>1</sup> has found the law according to which the current flowing from a point to a plane distributes itself over the area of the



plane. It seemed of some interest to see how the current would distribute itself to the various parts of a spherical surface from a discharging point situated at its center of curvature, inasmuch as the electrostatic field is much simpler in this case and

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#### JOHN ZELENY.

A brass cylinder was divided into the four parts A, B, C and D, which were separated by spaces of one millimeter and held in place by means of sealing wax. The cavity in the parts A, B and Cformed a hemisphere with a radius of 1.5 cm. The portions of the hemisphere on the three sections were of equal area. The effective areas of these sections for receiving the current, however, include parts of the air spaces between them, and as section B has air spaces on both sides, its effective area is about ten per cent. larger than that of section A. Section D was one centimeter in height and its interior surface was a cylinder three centimeters in diameter, thus forming a continuation of the spherical surface in the other sections.

The point P was a brass cylindrical wire .18 mm. in diameter. It had a rounded end which was placed at the center of the spherical surface in A, B and C. The auxiliary apparatus was the same as that used in the other experiments.

In taking readings each of the sections A, B, C and D was connected in turn to the galvanometer while the rest were joined to earth. The readings were taken with the apparatus in the open air, in the winter when the humidity was low, so that the results are but little different from what would have been obtained had dry air been used.

One set of readings taken for both the positive and the negative discharges is given in Table VII. The temperature was 21° C. and the air pressure was 74.8 cm.

# TABLE VII.

F	ositive	Dischar	ge.		N	egative	Dischar	rge.	
Voltage of Point.	Curr	ent in 19 Flow	o <sup>-7</sup> Amp ing to	eres	Voitage of Current in 10 <sup>-7</sup> A Point. Flowing to				eres
1	A	B	С	D		A	B	С	D
3,500	4.2	4.2	2.2		2,750	1.8	1.6	1.6	_
4,000	7.2	7.7	6.0	.06	3,000	4.4	3.9	3.5	-
5,000	15.4	16.5	14.9	3.3	3,500			10.2	3.0
6,000	26.4	28.6	26.4	10.7	4,000	15.4	17.1	16.5	8.3
6,500	33.0	_		_	5,000	32.1	36.3	34.7	26.4
7,000	39.8	42.9	40.7	20.9	5,500	45.1	50.6	48.4	39.6
Min. voltage	2.800	2.850	3.075		Min. voltage	2,550	2,625	2,625	3,075

#### Discharge to Different Parts of a Spherical Surface.



11. When due allowance is made for the inequality of the effective areas of the different sections as explained above, it is seen that the current is quite uniformly distributed over the whole surface of the hemisphere, for all but its smallest values. The effective area of B is about ten per cent. larger than that of A, and the currents going to it are larger by about the same amount. The effective area of C is also very likely somewhat larger than that of A, but as the upper air space is outside of the hemisphere it is more difficult to estimate its effect.

The values obtained by computing the current per square centimeter from the current flowing to the whole hemisphere, can be represented quite well for the positive discharge by the formula,

 $C = .60 \times 10^{-13} V(V - 2,800)$  amperes,

where V is the voltage of the point and 2,800 is the voltage at which the current started to flow to the central section.

• Similarly the negative current in amperes per square centimeter can be represented by

$$C = 1.23 \times 10^{-13} V(V - 2,550).$$

The values of the potential required to start a current in this case are nearly 200 volts smaller than is required to start a current from a point of the same size when placed at a distance of 1.5 cm. from a plane.<sup>1</sup>

The positive current flowing to the whole hemisphere at any voltage is not quite twice as large as would flow to a plane at the same distance, while the negative current flowing to the hemisphere is a little more than twice as large as the corresponding current flowing to a plane.<sup>2</sup>

Most of the current which flows to the section D at the higher voltages is due to a discharge from the side of the wire point, since owing to their high velocity it is not likely that many of the ions are forced out from the hemispherical volume by mutual repulsion.

When the section D was removed, the current received by section C was considerably smaller than that flowing to either A or B.

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<sup>1</sup> J. Zeleny, loc. cit., see Figs. 2 and 5.
<sup>2</sup> Ibid.
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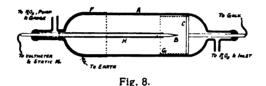
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#### JOHN ZELENY.

A small hole was bored in the center of a middle section of an apparatus similar to the above, and the pressure in the air was measured at that point during a discharge, by means of a sensitive manometer. The value obtained was about one third of that calculated <sup>1</sup> on the supposition that there are no convection currents. In the middle of the next section the pressure was still smaller.

# DISCHARGE AT DIFFERENT PRESSURES.

12. The results of some experiments which were carried out some time ago on the discharge from a point in dry air under pressures varying from that of the atmosphere to the very lowest at which a discharge could be made to pass, will now be described briefly.



The apparatus that was used is shown in Fig. 8, the auxiliary parts being practically the same as were used above.

The glass tube A, 4.6 cm. in diameter, contained the point B and the plate C. The point B consisted of a brass rod, 3.2 mm. in diameter, whose end was turned to a 15° cone, the diameter of whose point was .068 mm.

The rod was covered with the glass tube H, up to a distance of 1.6 cm. from the point. The brass plate C which received the current had a wire-gauze cylinder G attached to its rim. This protected the space between the point and the plate from the effects of any electrification that might collect on the walls of the glass tube. The distance between the point and the plate was one centimeter.

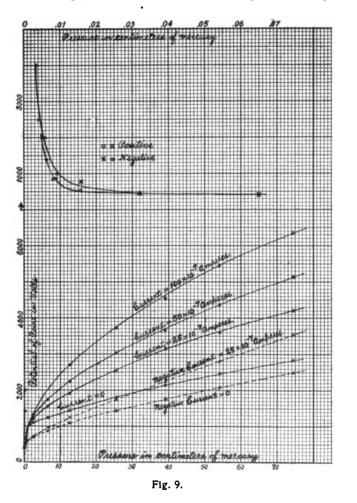
The part F of the glass tube was covered with earthed tinfoil to prevent the spreading over the outer surface of static charges from the high potential wire. A static machine was used for producing potentials above 1,000 volts, and a battery of storage cells was used for potentials below 1,000 volts.

Potential-current curves were obtained for both the positive and <sup>1</sup> A. P. Chattock, Phil. Mag., 48. p. 401, 1899.

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the negative discharges, for a large number of decreasing pressures until the discharge ceased to pass with the potential of the point at over 10,000 volts. The nature of the results obtained is shown by the curves in Fig. 9, which indicate how the potential required to



produce a given current changes with the pressure of the gas. The curves given were obtained from the potential-current curves for the different pressures, by plotting the potentials required at these pressures to produce the current stated in each case.

The full line curves are for the positive discharge and the two

broken line curves are for the negative discharge. The only values used in plotting the positive potential-current curves were those where the current was steady as indicated by the telephone receiver which was placed in the galvanometer circuit.

In considering the results it must be borne in mind that not only does the nature and the appearance of the discharge change as we reach the lower pressures, but in addition the area of the electrodes to and from which the discharge passes, increases until at the lowest pressures the current passed between the whole exposed surface of the point and the whole surface of the plate and the gauze cylinder attached to it.

At many of the low pressures the current would only begin with a high value, and as the voltage was diminished the current would drop as suddenly to zero.

It is seen from the curves in the figure that at the lowest pressures the current increases rapidly with change of voltage, since the potential-pressure curves for the different currents converge very rapidly for pressures below five centimeters, and below one centimeter the different curves are not distinguishable on the scale used.

For the positive discharge the voltage required to produce a current changes rapidly from about 1,000 volts for a pressure of one centimeter to a minimum of about 400 volts. With the negative discharge, for the same range of pressure, the voltage only changes from about 600 to 400 volts, the minimum voltage being the same as for the positive.

The curves in the upper part of Fig. 9 show how, at the lowest pressures used, the voltage required to produce a current changes with the pressure. It is seen that for a considerable range of pressure the voltage remains about constant and the same for both kinds of discharge, but that as the pressure is diminished below .01 cm. the potentials rise rapidly for both discharges.

With the positive discharge no current could be obtained with over 12,000 volts when the pressure was reduced to .0042 cm., while for the positive discharge when the pressure was as low as

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positive or the negative discharge would take place at any pressure, is about 400 volts, which value approximates to the cathode fall of potential in air which is observed in vacuum tubes where larger sized electrodes are used.

13. The general luminous aspect of the steady positive discharge at the different pressures will now be described.

(a) The light was confined to the immediate neighborhood of the point, appearing as a violet tinted speck of light, for all pressures down to 6.5 cm., at which pressure a violet glow extended back over the point for a distance of about two millimeters, the light at the point itself being more intense than that farther back.

(b) At a pressure of 2.5 cm. this glow had already spread back over the whole exposed surface of the point (1.6 cm.).

The discharge at this pressure would usually start with an instantaneous flash of light, consisting of a bright speck of light on the point itself, with a brush of light extending nearly to the plate, where a dark space separated it from a luminous coating on the plate itself. After this one flash, the appearance of the discharge changed to the violet glow over the point, described at first. When the static machine was stopped, the current gradually diminished and just as the discharge ceased a flash similar to that at the beginning would pass through the tube.

Sometimes the current continued intermittent, having to the eye the general appearance described for the flash discharge. At other times, again, a combination of the steady and intermittent discharges was noticed. These may not have been simultaneous, the discharge possibly alternating rapidly between the two kinds.

(c) At a pressure of .9 cm. the appearance of the steady discharge was the same as at 2.5 cm. pressure. Once at this pressure the current alternated back and forth between the steady and intermittent kinds described under (b), being intermittent for 20 seconds and then steady for 45 seconds, for a period of over 20 minutes, when the current was discontinued.

This indicates that during one of the discharges some surface condition necessary for its existence is altered by the discharge, so that the discharge changes to the other kind during which the original surface condition is recovered, enabling the discharge to change back again to the first kind.

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(d) At a pressure of .39 cm. the glow over the whole point had become somewhat wider than it was in the last case, being now about one millimeter wide and fading off into the gas.

(e) At a pressure of .19 cm. the glow over the point was still less sharply defined and extended for about three millimeters into the gas.

(f) With the pressures at .065 cm. and .032 cm., the glow extended out over half way to the plate and gauze, its exterior surace taking somewhat the outline of these two. There was now a reddish glow on the surface of the plate.

(g) At a pressure of .015 cm. there was a glow throughout the whole tube, except for a curved dark space near the middle of the volume.

(h) At a pressure of .0088 cm. and up to the limit when the discharge would no longer pass, the tube was filled with light of a bluish tinge, with a whitish glow on the point; and the discharge was intermittent.

The negative discharge at the low pressures was for the most part intermittent, and a few peculiarities only will be noted.

At a pressure of 2.5 cm. there was a considerable time interval between the application of the voltage (storage cells being used) to the point and the beginning of the discharge, being at times as much as eight minutes. When a glass tube containing one gram of one per cent. radium bromide was placed near the tube, however, the discharge always commenced immediately on applying the voltage.

At a pressure of .9 cm. a reddish spot of light, five to eight millimeters in diameter, appeared on the extreme edge of the wire gauze, with a corresponding spot on the point opposite. These spots of light rotated irregularly about the axis of the tube keeping more or less together. They seemed to be part of an arc discharge. At lower pressures down to .19 cm. these spots became more and more extended and diffused, finally appearing to envelop the whole point

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# GENERAL REMARKS.

14. It is of some interest to compare the potentials required to start a discharge from the three classes of points which have been studied. Such a comparison is made in Figs. 5 and 6, where, under the potential-diameter curves for C = 0, are drawn in broken lines the corresponding curves for needle points (taken from Figs. 2 and 3), and for cylindrical wires (taken from Figs. 2 and 5 of the previous paper — loc. cit.).

The comparison shows how much easier it is to start a current from the cylindrical wires than from the other points of like diameter. And while much finer needle points can be obtained than the diameters of the smallest wires, still the discharge from the fine wires takes place at considerably lower voltages than it does from the finest needles. The wires are preferable, too, because the fine needle points become blunter with use, while the wires of necessity do not. The formation of oxides on steel points, especially during the positive discharge, is also a disadvantage.

For the sake of comparison, the formulæ which have been found to represent best the experimental results for the positive currents from all of the points tried in each of the different cases, are here brought together. The distance between the point and the plane was 1.5 cm. in each case.

 $C = 2.58 \times 10^{-13}$  (1 + .110d) V(V - M) for cylindrical wires with hemispherical ends.

 $C = 2.60 \times 10^{-13}$ (1 + .30*d*) V(V - M) for cylindrical wires with plane ends.

 $C = 2.58 \times 10^{-13}$ (1+.319*d*) V(V-M) for steel needle points.  $C = 2.49 \times 10^{-13}$ (1+.176*d*<sup>3</sup>) V(V-M) for 12° conical points.

The values of the minimum potentials (M) in the four cases are given in turn by, 755 + 5.465d; 705 + 5.670d; 2.590 + 4.750d; and  $1.980 + 5.200d^{\frac{3}{2}}$ .

The initial constants in the current formulæ are quite alike, but there is much variation in the way that the current and the minimum potential depend upon the diameter of the point. The range of diameters used was different for the different cases and so the limits over which the formulæ have been tested are not alike.

#### JOHN ZELENY.

The beginning of a discharge from a point and the smaller currents from it, are often subject to considerable irregularity, especially if the discharge is negative. Some irregular resistance is present in these cases on the surface of the point, due perhaps to a condensed layer of gas on the metal surface hindering the free passage of the ions to and from the surface. The exposure of the point to radiations, like those from radium, removes the irregularity completely in some cases and partly so in other cases. It may be that the ions formed by the radiations in the condensed layer, moving under the action of the strong electrostatic field, are able to break up this surface layer more or less completely.

There is much less trouble with the larger currents from the point, possibly because the heat generated by the discharge dissipates the gas layer. Nevertheless when a large negative current from a point is reduced to a small value the irregularities become more pronounced than before and often a higher voltage is now required to start the current than was necessary in the first place.

This applies to the brass and steel points used in these experiments, and it is possible that some new effect is added due to an oxidation of the point or some other condition produced by the heating effect of the discharge. Users of platinum points have found, on the contrary, that often the potential at which a current stops is smaller than that at which it began, and hence in this case the gas layer may have been removed by the discharge and no new resistance introduced.

The reason why the positive discharge is on the whole so much more regular than the negative, may be due to the greater facility with which the smaller negative ions, produced by collision outside of the gas layer, penetrate the condensed layer and get to the metal surface.

The value of the minimum potential has been taken throughout as the lowest potential at which a current could be detected flowing from the point. The points have in all cases been exposed to the radiation from radium, and the potential at which a positive current was first observed to begin, as the voltage was gradually increased, was the same as that at which the current ceased, as the voltage was diminished. The smallest difference of potential that could be observed with the voltmeter used was about 25 volts.

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When the results for the negative discharge were not completely consistent, it was deemed advisable to use for the purpose of calculation those which showed the current to flow most easily, as they were the most free from the disturbing resistances which have been discussed. As already stated these results were those that were first taken with the point, before it had been used with large currents.

A formula, such as has been used to represent the potential-current curves, assuming as it does a gradual increase in the current from the beginning, as the voltage is raised, is better adapted to represent results for the simplest conditions obtaining at a point, than does one where a discontinuous rise of current at the start is assumed.

#### SUMMARY.

15. (a) Results are obtained from which it is possible to find the current that would flow in dry air to a plane 1.5 cm. distant, from points of any diameter, at any potential, when these points are either steel sewing needles of the usual taper, or  $12^{\circ}$  cones.

(b) The potential required to start a discharge from a point of any diameter and the current flowing from any point at any potential, can each be represented by a formula, for the positive discharge from either of the two kinds of points mentioned.

(c) The potential required to produce a current from the finest needles or cones, is considerably greater than is necessary when fine cylindrical wires are used.

(d) Masses of iron oxide form at the tips of steel needles during the positive discharge from them, and to a much less extent during the negative discharge.

(e) The negative discharge from the points shows considerable irregularity, especially for the smaller currents.

(f) The current flowing to a spherical surface from a point placed at its center of curvature distributes itself quite uniformly over the whole surface of the hemisphere opposite.

(g) With diminution of pressure the discharge between a point and a plane (distance = 1 cm.) takes place at gradually lower and lower potentials, and the current increases more and more rapidly with change of voltage. Below a pressure of one centimeter the potential required for the discharge drops rapidly to about 400 volts as the pressure is reduced to a few hundreths of a centimeter, and then at about a hundredth of a centimeter it begins to increase again rapidly.

Physical Laboratory, University of Minnesota, November 8, 1907.



# THE FLUORESCENCE AND ABSORPTION OF ANTHRACENE.

BY LOUISE SHERWOOD MCDOWELL.

A NTHRACENE, because of its intense blue-violet fluorescence, offers a promising opportunity for the comparative study of the fluorescence of a substance in its different forms : solid, liquid, and solution. The present study was undertaken, in order to make such a comparison, at the suggestion of Professors Nichols and Merritt, of whose inspiring interest the author wishes to express her grateful appreciation. Owing to the impurity of the anthracene used, the work naturally fell into three divisions : (1) the study of the fluorescence of impure anthracene; (2) the purification of the anthracene; (3) the study of the fluorescence of pure anthracene.

# NATURE OF ANTHRACENE.

Anthracene is a benzene derivative, prepared from those portions of coal tar which boil between  $340^{\circ}$  and  $360^{\circ}$  C. In its pure form the anthracene crystallizes in monoclinic plates, and has a blueviolet fluorescence. It melts at  $213^{\circ}$  C. and boils at  $351^{\circ}$  C. The crude anthracene contains an impurity of unknown composition, chrysogen, the slightest trace of which has been supposed entirely to destroy the blue-violet fluorescence.

#### HISTORY.

No study of the fluorescence of the crude anthracene has, so far as the writer is aware, yet been undertaken. The study of the fluorescence of the pure anthracene has been chiefly confined to the solutions. In this field, the work of two men needs to be mentioned, J. Hartley, in England, and O. Knoblauch, in Germany. Hartley<sup>1</sup> studied the absorption bands of solutions of pure anthracene in glacial acetic acid diluted with absolute alcohol. The solutions varied in concentration from 1 part of anthracene in 1,000 of the

<sup>1</sup> Hartley, J., Journal Chemical Society, 39, 162.

solvent to 1 part in 50,000,000. He found four absorption bands in the following positions :  $\lambda$ .3600-.3607  $\mu$ ; .3430-.3434 $\mu$ ; .3285-. .3287  $\mu$ . The least refrangible was not measurable on his scale.

O. Knoblauch,<sup>1</sup> in a general study of the intensity of fluorescence of various solutions, studied ten solutions of pure anthracene, which he arranged in order of intensity of fluorescence, as follows : benzol = toluol = xylol = isobutyl alcohol > amyl alcohol = ethyl alcohol = ether > acetone > petroleum ether > chloroform.

In this country E. L. Nichols and E. Merritt,<sup>2</sup> in a study of the fluorescence and phosphorescence of various organic substances at low temperatures, have found that, at the temperature of liquid air, the solid still shows the characteristic blue-violet fluorescence unchanged in intensity, and also a white phosphorescence.

Within the past year, T. S. Elston<sup>3</sup> has made a study of the fluorescence of the vapor of pure anthracene and found that the fluorescence spectrum extends from  $\lambda$ .365 to .470  $\mu$ , with bright bands at  $\lambda$ .390, .415, and .432  $\mu$ , and that the absorption spectrum extends continuously from about  $\lambda$ .400  $\mu$  to some point beyond  $\lambda$ .325  $\mu$ .

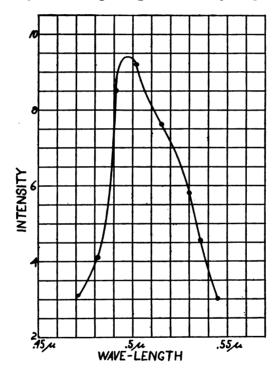
FLUORESCENCE OF IMPURE ANTHRACENE.

The present experiments were begun with a partially purified, crystallized anthracene, yellow in color. This showed a bright green fluorescence. To put in convenient form for photographing, the anthracene was melted between two microscope slides, and allowed to cool. The layer so formed was about a millimeter in thickness. In this form the anthracene showed three distinct absorption bands, the position of which was found photographically. The plate was placed close to the tube of the spectrograph; the carbon arc light focused upon it; and an exposure of ten to twelve seconds made. Of the five exposures on each plate, the first and fifth were of the potassium and strontium arcs respectively. By means of these two reference spectra, a calibration curve was plotted, and the position of the absorption bands read from the curve. See plate at close of article. The bands were found to have the following positions :

> <sup>1</sup> Knoblauch, O., Wiedemann's Annalen, 54, 192. <sup>3</sup> Nichols and Merritt, PHYSICAL REVIEW, 18, 355. <sup>3</sup> T. S. Elston, Astrophysical Journal, April, 1907.

Extent.	Middle Point.
λ	λ
4,990-4,870	4,930
4,620-4,520	4,570
4,215-	

For the fluorescence, the mercury arc lamp of the Arons Lummer type was used as an exciting light, and also as a reference spectrum. The first four exposures on each plate were of the fluorescence spectrum, for which the apparatus was so arranged that the spectrograph and lamp were at right angles and the plate placed with its



edge vertical and directly in front of the slit of the spectrograph. For the fifth exposure, the light of the mercury arc was reflected directly into the spectrograph by a glass mirror placed at an angle of  $45^{\circ}$ . The time of exposure varied, according to the width of slit, from five minutes to an hour. In order to test the effect of the glass, one photograph was taken in which the plate was replaced by a solid cylinder of anthracene about .8 cm. in diameter; and the

light from the mercury arc was passed through a violet glass to cut off the green light. The resulting photographs show two fluorescence bands, of which the first is but faintly visible in the photograph, although it appears to the eye the more intense. See plate at close of article. The position of the bands is :

	~
Band I.	5,440-5,250
Band II.	5,145-4,865

A photograph of the fluorescence of solid methyl anthracene taken in the same way showed these two green bands, and in addition a faint blue fluorescence extending to line  $.4358 \mu$  of the mercury spectrum.

As a check upon the results obtained photographically, the intensity curve for the green fluorescence bands was taken by means of a Lummer-Brodhun spectrophotometer. The iron spark was used as an exciting light. In order to avoid stray light, the visible portion of the spectrum, formed through a quartz lens and prism, was intercepted by a screen, and only the ultra-violet rays allowed to fall upon the plate of anthracene. In this case the plate was formed by subliming the anthracene on glass. As a comparison light there was used an acetylene flame reflected at an angle of about 45° from a block of magnesium carbonate. To prevent light from this source falling on the plate the acetylene flame, except for the circular opening through which light fell upon the reflecting surface, was completely enclosed by a black screen. The results are shown in the accompanying curve. To test the killing effect of the extremered and infra-red rays upon the green fluorescence, the light of the arc lantern was intercepted by a thin rubber screen, and the rays which passed through allowed to fall at grazing incidence upon the fluorescing surface. The intensity of the fluorescence as observed through the spectrophotometer remained unchanged.

For the determination of the rays which excite the green fluorescence of the solid, the spectra of the carbon arc lamp, the mercury arc, the Nernst glower, and the iron spark, were successively thrown on a screen, and the plate of sublimed anthracene moved slowly through the spectrum. In the last case, the spectrum was produced by a quartz lens and prism, to avoid the absorption due to glass. The results show that, with the possible exception of two narrow bands in the blue, all rays are effective from the green to the extreme ultra-violet.

The study of the fluorescence of the liquid anthracene involved several difficulties. The anthracene, if melted too rapidly, decomposes; also it begins to sublime at temperatures far below the melting point, and if removed from the heat, coats over the surface before an observation can be taken. To obviate these difficulties. the anthracene was placed in a long glass tube about one and one half centimeters in diameter, and placed in an electric heater,  $6 \times 6 \times 1$  in. The whole was covered with asbestos paper, except for openings through which the tube and thermometer were received, the light admitted, and observations taken. For the absorption bands, both a gas flame and a focused carbon arc were used, but no absorption bands were visible through the spectroscope. Throughout the experiment, the thermometer was kept only a few degrees above the melting point, yet the solution under the influence of the heat rapidly decomposed, turned orange, and then dark brown until it became almost opaque to light. For the fluorescence the plan was first tried of sealing the metal terminals for a spark into the glass tube, but the anthracene vapor attacked the terminals and caused them to burn out so rapidly that the plan had to be abandoned. Thereafter the spark was placed just outside the glass tube. Under these conditions, the liquid showed no fluorescence when excited by the spark between terminals of aluminum, zinc, tin, or iron, by the mercury vapor lamp, or the carbon arc.

To test the fluorescence of impure anthracene in solution, the following solvents were used : benzol, toluol, xylol, isobutyl alcohol, amyl alcohol, ethyl alcohol (absolute), ether, acetone, petroleum ether, chloroform, carbon disulphide, and glacial acetic acid. Concentrated solutions were first made and then diluted in the ratios 1:2, 1:4, 1:8, 1:16, 1:32. In ether and acetone solutions, through cells three centimeters thick, there were visible very faint absorption bands, too faint to affect the photographic plate when exposures for 25 minutes were made. In this case the light was that of the ordinary gas burner. No fluorescence was observable under any of the excitations previously tried. In testing the exciting powers

of the ultra-violet rays small rectangular glass cells  $5.65 \times 3 \times 1$  cm. (inside measurement) were nearly filled with the solution to be tested; the open top covered by a quartz plate; and the metal sparks of aluminum, zinc, tin, iron, and copper successively placed above. In no case was fluorescence visible.

### PURIFICATION OF ANTHRACENE.

In the course of the determination of the exciting rays, an attempt was made to use plates prepared by evaporating a chloroform solution on glass. When a plate so prepared was held in the ultraviolet spectrum of the iron spark it fluoresced, but with a faint blue color, suggestive of pure anthracene. A similar test of other solutions, which had been standing in a dimly lighted room for several days, gave the following results :

Chloroformblue.
Xylolblue-violet.
Isobutyl alcoholblue-green in center, blue on edge.
Toluolblue-green.
Amyl alcoholgreen.
Absolute alcoholgreen.
Acetonegreen.
Ethyl ethergreen in center, blue on edge.
Glacial acetic acidgreen in center, blue on edge.
Benzolgreen in center, faintly bluish green on edge.
Carbon disulphidegreen in center, faintly
bluish in spots, usually yellowish white, non-fluorescent on edge.
Acetoneyellowish green in center, faintly blue-green or green on edge.

Obviously the next step was to decide the relative effects of solvent, concentration, light, and time, in producing the change. For this purpose fresh solutions, saturated and dilute, were made in the most promising solvents : chloroform, xylol, and isobutyl alcohol. Portions of these solutions were left in diffuse daylight and in a photographic dark room. Each day for a week, tests were made by evaporating small portions on glass and placing the evaporated product in the light from the carbon arc, and also from the iron spark. The tests showed :

I. That daylight assists the change although bright sunlight is not essential.

II. That solvents differ in their ability to produce the change, i. e., xylol is better than chloroform.

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No. 2.] FLUORESCENCE AND ABSORPTION OF ANTHRACENE. 161

III. That a difference in concentration has little effect upon the change.

IV. That the time required depends upon the brightness of the light and the solvent used.

V. That in some cases the evaporated product, if exposed to air, decomposes.

These results led to a study of the method of Fritzsche,<sup>1</sup> who was probably the first to undertake the purification of anthracene. His method in brief was this: The crude anthracene was dissolved with heat in a mixture of coal-tar oils (Steinkohlenoel) and placed in the sunlight. The substance which first crystallized out was dissolved in the same way until crystals of the desired purity were obtained.

Berthelot's <sup>2</sup> method is similar. The coal-tar product left in the retort by the distillation of the substances which boil below  $350^{\circ}$  is crystallized again from boiling xylol, and each time the part which crystallizes out on cooling, is pressed out. Then it is again crystallized from alcohol, and finally sublimed at the lowest possible temperature.

In the first experiments performed by the writer, the impure anthracene was dissolved in boiling kerosene, and the saturated solution allowed to stand in sunlight until a portion crystallized out. These crystals were redissolved in fresh kerosene, and the process repeated until the product was very nearly pure white. After the last filtration, the anthracene was washed in cold alcohol, in which it is but slightly soluble. To test the effect of the fresh kerosene, the product which first crystallized out was redissolved in the same solution, allowed to crystallize out a second time, and the process repeated until the yellow color disappeared. The precipitate was finally filtered out and washed as before. No difference in the product so obtained was observable. As a third test, the hot solution of anthracene was kept in the sunlight for fifteen minutes, at a temperature which prevented crystallization; then allowed to crystallize; filtered out, and the precipitate washed in alcohol. Since this product when subjected to the tests described below showed

<sup>1</sup> Fritzsche, Zeitschrift für Chemie, 1867, p. 290.

<sup>2</sup> Berthelot, Bulletin de la Société Chimique de Paris, 8, 232.

the greatest purity of all the kerosene treated products, it is evident :

I. That renewal of solvent is unessential.

II. That repeated crystallization is unessential.

The same method was tried with chloroform and xylol. An attempt to substitute arc light for sunlight showed that owing to the lessened intensity of the light a much longer time was required.

To the products thus purified, various tests were applied. Thev were found to possess a blue-violet fluorescence, and to dissolve readily in any of the solvents used, giving solutions with a blueviolet fluorescence. The xylol and chloroform products, if not carefully washed, gradually lost their fluorescence and turned a yellowish brown. Sublimation of the products in air showed that the chrysogen was still present, for the sublimate gave in one spot blueviolet fluorescence; in another, green. When the sublimation was gentle, that which was first deposited on the cold plate of glass showed blue-violet fluorescence. As the heat increased the later deposit showed green fluorescence, so that, by illuminating the plate from the one side or the other, the blue-violet or the green fluorescence was obtained. By stopping the gentle sublimation at the proper time, a product was obtained which gave only blue-violet fluorescence, while the rapid sublimation of the residue gave a product of which the green fluorescence was more intense than any yet observed. Apparently by this means there was secured a greater concentration of the chrysogen, although a complete separation was not effected.

To test whether the change in color of the fluorescence was due to the heat to which the product was subjected, the blue-violet sublimate was rapidly resublimed and gave still a blue-violet fluorescence, which grew gradually fainter as the amount of the sublimate was lessened by repeated sublimations. To complete the separation of the pure anthracene the kerosene-treated product was sublimed in a partial vacuum. The crystals were placed in the bottom of a cylindrical tube. About two inches above was a wire triangle, upon which rested a small glass plate. The tube was connected to a mercury pump and exhausted as far as possible, then closed and placed in a bath of salt and water maintained approximately at 100° C. The sublimation was allowed to continue for about two hours, then the plate was removed and tested. By this means regular crystals of pure anthracene were obtained, and in the later fractions somewhat irregular fern-like crystals, the form of which was apparently modified by the presence of the chrysogen. Complete separation of the chrysogen was not effected. An attempt to separate the pure anthracene by sublimation, before treatment with the kerosene, proved unsuccessful.

To account for these results one possible explanation suggested itself, an explanation based upon the following known facts:

I. Anthracene, if allowed to stand in solution in the bright sunlight, gradually goes over into dianthracene  $(C_{28}H_{20})$ , which melts at 244° C., but upon melting reverts to anthracene, the melting point of which is 213° C.

II. Chrysogen is known to go through an apparently similar transformation, since if ordinary white dianthracene, which has a blue fluorescence, is melted, the resulting product is yellow and fluoresces bright green.

May it not be that, when the anthracene is exposed to sunlight, the chrysogen first goes over into dichrysogen so that the product which crystallizes out is a mixture of anthracene and dichrysogen, and that the latter upon sublimation at high temperatures reverts to chrysogen and thus restores the green color? This would explain the greater ease of separation after the product is crystallized out of solution.

THE FLUORESCENCE AND ABSORPTION OF PURE ANTHRACENE.

In the study of the fluorescence of the solid, a comparison was made of the fluorescence of the original yellow anthracene, the bright green product of rapid sublimation, the blue-violet product of gentle sublimation, and the pure anthracene crystals from the sublimation in vacuo. As exciting lights, the mercury arc and the ultra-violet rays of the iron spark spectrum were used. As before, the method was photographic. For the absorption bands, the light of the carbon arc lamp was focused upon the plates as in the case of the impure anthracene. For the iron spark excitation the ultraviolet rays were allowed to fall on the plate, and the visible spectrum intercepted by a screen. Tables I. and II. give the results of the comparison. A question mark in a column indicates that owing to the presence of a mercury arc line, the exact position of the band is uncertain. The last two bands are those obtained for the fluorescence of the impure anthracene. These results indicate that the substance is fluorescent in all stages of the purification, and that the blue-violet fluorescence is not entirely killed by the presence of the chrysogen. In the purer

IABLE I.	T	AB	I.E	I.
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Substance.	Time.			Bands.			Fxtent.	Excitant.
G.S.	30 min.	?			5,010	5,310	4,860-5,370	M.A.
O.S.	30 "	4,358			5,010	5,310	4,130-5,370	"
<b>B.</b> + <b>G</b> .	45 "	4,358	i		4,985	5,310	4,130-5,370	"
<b>V.B.</b>	90 "	4,358	I	4,730	4,985			"
G.S.	45 ''				4,975	5,280	4,850-5,375	"
<b>B.</b> + G.	90 **	4,358	1	1	4,980		4,140-5,080	**
G.S.	75"	4,250	4,510	4,750	4,960		4,190-5,060	U.V.
0.S.	60 ''	4,260	4,490	4,750	4,980	1	4,190-5,090	**
V.B.	120 "	4,260	4,490	l .	4,960		4,190-5,030	**
<b>B.</b> + G.	60 ''	4,260	4,510	l	4,960		4,190-5,060	"
P.A.	120 "	4,220	4,470				4,100-4,750	**
<b>O</b> .	120 "			:	4,940		4,870-5,010	"

Fluorescence of Solid Anthracene of Different Degrees of Purity.

TABLE II.

Position of Absorption Bands of Solid Anthracene.

Substance.	Time.	Width of Bands.				
O.S. '	12 sec.	4,090-	4,840-4,900	4,540-4,615		
G.S.	20 ''	4,090 -	4,860-4,925	4,570-4,650		
B. + G.	20 ''	4,090-				
V. B.	25 ''	4,100-	1			
V. B.	25 ''	4,100-	I			

G.S. = green sublimate.

O.S. = original anthracene sublimed.

B. +G. = blue and green sublimate.

- P.A. = crystals of pure anthracene.
  - $O_{\cdot} = original anthracene melted on glass.$
- V. B. == violet-blue sublimate.

M.A. == mercury arc.

U.V. = ultra-violet rays of iron spark.

Arc = carbon arc through glass.



specimens, however, the violet fluorescence was relatively strong, the green weak, and in the most impure products, the violet was so faint as to be barely visible. See plate.

For the study of the absorption and fluorescence of the solutions of pure anthracene, the kerosene-treated product was used. Small amounts of concentrated solutions in the following solvents were made, and diluted as described later : xylol, benzol, toluol, isobutyl alcohol, amyl alcohol, ethyl alcohol (absolute), ether, acetone, petroleum ether, chloroform. To test the effect of varying concentration upon the position of the fluorescence bands, the fluorescence bands of the xylol solutions with six different concentrations from } to  $\frac{1}{512}$  conc. were photographed. There was found to be no apparent shift of the bands with the concentration. The absorption bands of each solution in turn were then photographed, in the following way: The light of an acetylene flame was diffusely reflected from a block of magnesium carbonate at 45°; the solution to be tested was placed, in a glass cell I cm. in thickness, in the path of the reflected beam, and the spectrograph placed in contact with the cell. All direct light was shut off by a screen. As in other cases, the mercury arc spectrum was used for reference. As an additional precaution against shift with concentration, only dilute solutions were used, the solution in most cases probably being not more than  $\frac{1}{25\pi}$  conc. After each exposure, the solution was replaced by the plain solvent in a similar cell, and another exposure made in the same way. Table III. gives the results. The dash indicates that the band extends to the violet end of the visible spectrum.

For the fluorescence bands, the arc light was used. The mercury arc, and sparks of iron, copper, zinc, tin, lead, aluminum, cadmium, antimony, bismuth, silicon, and carbon, failed to give an exciting light sufficiently intense, even when placed directly above the cell at a distance of one inch, and separated from the solution by a quartz plate. In order to guard against the possibility of stray light, the cell was covered with black paper except for two opposite rectangular slits about I cm. wide, through which the beam of exciting light passed, and for a small circular opening at right angles to these and just fitting the lens of the spectrograph. Also the barrel of the spectrograph was covered with black paper, and

# TABLE III.

Solvent.	Time.	Bands.
Xylol 1/2 conc.	5 min.	4,080
Xylol 🕹 "	5"	4,080-
Xylol <sub>x</sub> 'r "	5"	4,080-
Xylol TIX "	5"	4,050-
Xylol zta "	5"	4,050-
Xylol xta "	5"	4,050
Benzol	5 ''	4,050-
Toluol	5 "	4,050-
Isobutyl alcohol	5"	4,050-
Amyl alcohol	5"	4,050
Absolute alcohol	5 "	4,050-
Ether	5"	4,050-
Acetone	5"	4,080-
Petroleum ether	5 "	4,080-
Chloroform	5"	4,080-

TABLE IV.

Solvent.	Time.	Bands.				Extent.	
X. <u>}</u> c.	60 min.	4,050	4,270	4,520		5,030-4,000	
X. i c.	70 ''	4,050	4,270	4,520		5,030-4,000	
Х. <mark>1</mark> . с.	60 ''	4,050	4,270	4,520		5,140-4,000	
X. $\frac{1}{32}$ c.	60 ''	4,060	4,300	4,570		4,970-4,000	
X. 🖧 c.	60 ''	4,060	4,300	4,570		5,030-4,000	
X. $\frac{1}{1^{2}s}$ c.	60 ''	4,060	4,300	4,570		4,970-4,000	
X. $\frac{1}{256}$ c.	60 ''	4,060	4,310	4,555		5,030-4,000	
B. 238	60 ''	4,060	4,310	4,570		5,030-4,000	
T.	60 ''	4,050	4,285	4,540		4,970-4,000	
I.A.	60 ''	4,030	4,260	4,540	?	4,970-4,000	
A.A.	60 "	4,030	4,250	4,500	4,810	4,970-4,000	
Ab.A.	60 "	4,020	4,260	4,500	4,760	5,030-4,000	
E.	60 ''	4,035	4,225	4,535	4,860	5,030-4,000	
Α.	60 "	4,040	4,250	4,535	4,860	4,980-4,000	
P.E.	60 ''	4,030	4,225	4,490	4,800	4,900-4,000	
Ċ.	60 ''	4,050	4,260	4,550	l	4,890-4,000	
X.	50 ''	4,060	4,290	4,585		4,900-4,000	
т.	50 ''	4,050	4,270	4,550		4,900-4,000	
X.	60 ''	4,050	4,290	4,535		5,000-4,000	

Position of Fluorescence Bands of Pure Anthracene in Solution.

had a black screen encircling it at a distance of about two inches from the cell, to prevent any possibility of reflected light entering the instrument.

Of the five exposures made on each plate, the first and third were of the fluorescing solutions, the second and fourth of the plain solvents, the fifth of the mercury arc. As was to be expected, the photographs of the plain solvents were almost blanks, showing the nearly total absence of stray light. In order to determine the exact position of the fluorescence bands, a calibration curve was drawn from the position of the mercury lines. Table IV. gives the results. The midpoint of each band and the total extent of the fluorescence are given in each case. A question mark indicates that the presence of bands in that column is doubtful. For the last exposure the iron arc was used as an exciting light. Otherwise the procedure was the same. See plate.

There was found to be no shift in the position of the bands either with a change in concentration or solvent. Table V. gives the average wave-lengths for the different bands of both pure and impure anthracene in the three forms. The figures for the vapor are those given by T. S. Elston.

# TABLE V.

Average Position of Fluorescence Bands.								
Solid.	4,250	4,495	4,745	4,980	5,300			
Solution.	4,050	4,275	4,540	4,820				
Vapor.	3,900	4,150	4,320					

The fluorescence bands occur, apparently, at equal intervals, with a distance between bands approximately equal to  $.025 \mu$ . With the change from solid to solution and solution to gas, there is a shift in the bands towards the shorter wave-lengths.

# SUMMARY.

The results of the study may be briefly summarized thus :

I. Commercial anthracene, in the solid form, possesses a fluorescence fully as intense as pure anthracene, but different in color. It consists of bright bands at  $.498 \,\mu$  and  $.530 \,\mu$ . The absorption spectrum consists of bands in the positions  $\lambda.499-.487 \,\mu$ , .462- $.452 \,\mu$ , and of a continuous spectrum from  $\lambda.4215 \,\mu$  to some point beyond the range of the apparatus. II. The blue fluorescence is not entirely destroyed by the presence of the chrysogen, but may with the proper excitation coexist with the green fluorescence.

III. The fluorescence of the pure anthracene, both solid and in solution, consists of distinct bands separated by regions of diminished intensity.

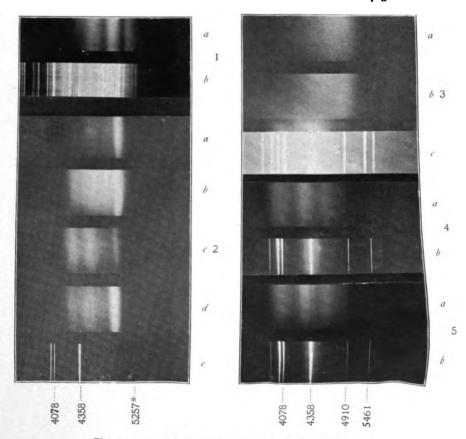
IV. In the case of the solid, there are three bands at  $\lambda.425 \mu$ , .450 $\mu$ , and .475 $\mu$ . In the case of the solution, there are three, possibly four, bands at  $\lambda.405 \mu$ , .4275 $\mu$ , .475 $\mu$ , and (?) .482 $\mu$ .

V. With the change from solid to solution and solution to gas there is a progressive shift in the fluorescence bands towards the shorter wave-lengths.

VI. The absorption spectrum of the pure anthracene is continuous from about  $\lambda.410 \,\mu$  to some point in the ultra-violet beyond the range of the apparatus. That of the solution is continuous from about  $\lambda.405 \,\mu$ .

PHYSICS LABORATORY, CORNELL UNIVERSITY.





PHYSICAL REVIEW, February, 1908.

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To face page 168.

Fluorescence and Absorption Spectra of Anthracene.

1. a, Absorption of solid commercial anthracene; b, Strontium.

2. Fluorescence of solid anthracene of different degrees of purity (see Table I.): a, Green sublimate; b, Commercial anthracene sublimed; c, Violet-blue sublimate; d, Blue and green sublimate; e, Mercury arc.



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# THE HEAT DILUTION OF AQUEOUS SALT SOLUTIONS.

#### By F. L. BISHOP.

THE following paper contains the description of a new method and form of calorimeter for certain thermochemical measurements: some determinations of the heat of dilution of solutions of sodium nitrate, potassium nitrate, potassium chloride, barium nitrate: and some conclusions on an analogy between this heatquantity and the Joule-Thomson effect and on the application of van der Waals's equation to solutions.

Although many investigators ' have already studied the heat of dilution of aqueous salt solutions, yet it seemed desirable to study

more thoroughly solutions at moderately low concentrations: this work was undertaken with that end in view.

Calorimeters. — This consists of two concentric cylinders Aand B, Fig. I. The inner one is suspended by the tube C by which it is rotated at a constant rate. This tube was for a part of its length made of hard rubber to avoid undue heat conduction. Vanes on the inside of the outer calorimenter and on the outside of the inner cylinder provide ample means for mixing

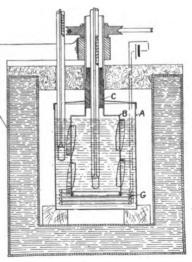


Fig. 1.

and agitating the liquids. The bottom of the inner calorimeter

<sup>1</sup> Among others reference may be made to the following: Thomsen, Thermochem.

was made so that it could be easily removed. This was accomplished by turning down the bottom of the cylinder until its wall was very thin and would spring a small amount. The bottom was accurately fitted to this and forced into it slightly until the joint was water tight. It was found that the bottom could be easily removed by pressing down on it with the thermometer.

The two liquids are mixed by dropping the bottom out of the inner calorimeter and at the same time lowering it until its top is below the surface of the liquid. Then the liquid is forced by the rotary motion of the inner calorimeter to pass up the outside and down the inside of the inner calorimeter, or if the direction of rotation is reversed, it can be made to circulate in the opposite direction.

A small piece of thin metal, not shown in the drawing, just large enough to move freely in the inside calorimeter, was fastened to the thermometer thus preventing the liquid on the inside from taking up a regular rotary motion and causing it to be very completely agitated so that it would assume the temperature of the liquid on the outside. The calorimeters were made of brass and covered before each experiment with a thin coating of bees' wax. Three different sizes of calorimeters varying from 2,000 c.c. to1,000 c.c. for the outside and from 700 c.c. to 300 c.c. for the inside cylinder gave a number of ratios of solvent to solute. The calorimeter was placed in a double-walled vessel filled with water and covered with two layers of inch felt, and the whole arrangement was placed in a tank of oil<sup>1</sup> kept at a constant temperature.

The difference in temperature was measured by Beckmann thermometers which read directly to hundredths of a degree. Instead of determining the heat-capacity of the apparatus a difference of temperature nearly equal to that obtained in the dilution experiments was reproduced by means of an electrical heating coil G, Fig. I, and the relation between rise of temperature and electrical energy expended was determined. A number of different forms of this heating coil were used. One was made by drawing a bare

<sup>&</sup>lt;sup>1</sup> For a description of this constant temperature tank see A Method of Determining Thermal Conductivity, by F. A. Laurs, F. L. Bishop, and P. McJunkin, Proc. Am. Ac. of Arts and Sciences, Vol. XLI., p. 455.

german-silver wire into a capillary glass tube and then coiling it into the desired shape. Another and one of the most satisfactory was made by using small copper tubing and insulated wire. The input of electrical energy was measured by a Weston Laboratory standard ammeter and voltmeter and the time by a stop watch.

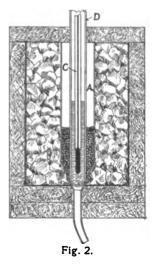
All the instruments used in the final readings were carefully calibrated, the thermometers had been compared by the Reichsanstalt, and the electrical instruments were compared with a Carhart-Clark cell by means of a potentiometer. Preliminary experiments were made to determine the best size of calorimeters to give the various quantities such magnitudes that they could be read to 0.1 per cent. with the exception of the temperatures, and the mean of these is in most cases approximately that.

This form of calorimeter reduces the error due to radiation to a minimum since there is only one calorimeter exposed to radiation. This error could be completely eliminated by causing the liquids to mix at a slower rate and supplying electrical energy at such a rate there would be no change of temperature. In the cases where heat is given out it is only necessary to cool the liquids by a suitable arrangement to the temperature existing before mixing and then applying the electrical energy to reproduce the same temperature.

This method also avoids the necessity of determining the heat-capacity of the liquids and of the calorimeter and insures that the two liquids shall be at the same temperature when mixed.

Tests of the Calorimeters. — In order to show that the electrical method gave the actual heat change when the liquids were mixed, certain metals whose heat-capacity are well known were investigated with the help of the apparatus shown in Fig. 2.

The apparatus consists of a vessel holding a certain amount of metal which is surrounded by a second vessel containing ice. The inner vessel has a conical bot-



tom terminating in a short glass tube through which the metal falls

into the center of the calorimeter. This is closed by the glass tube D which also serves the purpose of holding a thermometer surrounded by mercury thus insuring that the metal in A is at the same temperature as the ice in the surrounding vessel. The whole is surrounded and covered by a double layer of felt.

This apparatus was placed over the calorimeter with the cone extending through the opening in the top of the outer part of the calorimeter in place of the thermometer. The inner cylinder was used without its bottom and with its top below the surface of the water so that it served simply to agitate the liquid.

A quantity of the metal was used which would give the same lowering in temperature as that given by mixing the liquids in the dilution experiments. This metal was allowed to stand surrounded by the ice until it was at the same temperature as the ice. Since the metals were reduced so much below the dew point it was necessary to dry the air surrounding the metal and to prevent the circulation of any fresh air around the metal by closing the outlet tube and covering the top. Meanwhile the water in the calorimeter was adjusted to constant temperature, after which the metal was allowed to pass into the water and the temperature and rate of radiation noted. Then the same temperature was reproduced by the electrical energy.

The six tests of the calorimeter made in this way are shown in the following table where column I. gives the metal used, II. the amount of heat as computed from the heat-capacity and the change in temperature of the metal, III. the amount of heat supplied electrically. The difference in the amount of heat shown for different tests indicates that different size calorimeters, were used. The first and second experiments should be considered as preliminary.

11.	III.
2,473	2,406
2,378	2,434
1,993	1,995
2,004	2,006
2,295	2,285
2,344	2,322
	2,473 2,378 1,993 2,004 2,295

being checked by evaporating to dryness a small portion of the resulting solution and weighing the residue. The substance as received chemically pure was recrystallized and tested for the ordinary impurities.

The following set of readings shows the character of the observations and indicates the change of the different quantities with the time during a run and the change in temperature due to radiation from which the correction for it was deduced. Readings of only one of the thermometers is here given. The readings were taken every minute. All the determinations were made at  $25^{\circ}$  C.

Run No. 16. Potassium Chloride. July 10, 1907. 2, 192 Grams of Solution, Concentration 4.492. 294.2 Grams of Water.

Temperatures.			1		1
Before Mixing.	After Mixing.	After Applying Electricity.	Amperes.	Volts.	Time in Seconds
3.409	3.220	3.414	2.755	2.688	268.7
3.409	3.221	3.417	2.755	2.688	
3.409	3.222	3.417	2.754	2.687	1
3.409	3.2225	3.417	2.752	2.685	1
	3.2235	3.418	2.752	2.685	
	3.224	3.418	2.752	2.685	

Temperature decrease produced by mixing 0.192 corrected for radiation. Temperature increase produced by electricity 0.194.

Resulting concentration 3.808 mols per liter of water.

Heat 48.71 calories per gram-mol.

In the following table of results column I. gives the amount of the solution in grams; II., the concentration of this solution in gram-molecular weights in 1,000 grams of water; III., the weight of water added; IV., the concentration of the resulting solution; V., the decrease of temperature corrected for radiation, when the solution was diluted; VI., the increase of temperature when the electrical energy was applied; VII., the electrical energy used in joules; VIII., heat in calories per gram-molecule of salt attending the change in concentration shown by columns II. and IV.; IX., the total heat absorbed when that quantity of solution containing one mol was diluted from the highest concentration to the concentration in question.

# F. L. BISHOP.

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1.	п.	111.	IV.	<b>v</b> .	VI.	VII.	VIII.	IX.
2,240	2.380	284.3	2.049	0.270	0.260	2,212	129.9	129.9
2,110	2.028	305.1	1.750	0.215	0.200	1,664	119.1	264.1
1,682	2.380	826	1.550	0.572	0.547	4,410	341.1	341.1
2,054	1.750	287.1	1.500	0.181	0.193	2,341	116.9	381.0
2,035	1.500	303.0	1.280	0.140	0.136	1,192	110.2	491.2
813	1.576	1,031	0.637	0.315	0.309	1,802	397.5	743
797	1 578	1,505	0.493	0.289	0.273	1,991	462.9	808
330.2	2.380	1,908	0.291	0.331	0.331	2,455	920	920
			Sodiı	ım Nitra	te.			
828	2.172	312.0	1.500	0.305	0.225	887	189.2	189.2
842	2.172	314.8	1.510	0.305	0.244	961	185.1	185.1
769	1.500	305.1	1.040	0.174	0.174	711	165.8	355.0
334.5	2.172	752	0.593	0.331	0.269	1,058	507	507
305.7	1.500	747	0.400	0.177	0.179	822	404.7	594
314.2	1.510	747	0.409	0.175	0.174	685	<b>392.</b> 0	581
			Bari	um Nitra	nte.			
792	0.705	291	0.506	0.068	0.078	347	144	144
827	0.705	291	0.510	0.078	0.077	277	138	138
819	0.705	300	0.503	0.053	0.061	257	153	153
776	0.506	295	0.360	0.040	0.036	173	128	170
801	0.510	302	0.286	0.044	0.043	271	191	·329
301	0.705	756	0.191	0.075	0.070	312	409	409
297	0.506	751	0.137	0.043	0.077	347	306	450
			Polass	ium Chlo	ride.			
2,190	4.492	296.0	3.804	0.182	0.198	1,612	48.0	48.Ò
2,192	4.492	294.1	3.808	0.192	0.194	1,521	48.7	48.7
1,690	3.804	284.6	3.127	0.179	0.181	1,185	55.8	103.8
1,595	3.127	286.5	2.564	0.124	0.130	836	47.1	150.9
1,498	2.564	305.0	2.053	0.102	0.115	718	46.1	197.0
1,496	2.053	297.5	1.670	0.075	0.072	473	44.1	241.1
342.0	4.492	1,456	0.673	0.256	0.263	1,845	372.6	372.6
338.1	4.492	1,456	0.666	0.254	0.232	1,683	384.8	384.8
338.3	4.492	1,862	0.218	0.217	0.538	1,876	395.7	395.7
796	1.461	285	0.058	0.070	1.05	318	60.0	306
776	1.05	293	0.036	0.050	0.74	231	53.0	358
310	1.461	762	0.062	0.067	0.39	318	173	418

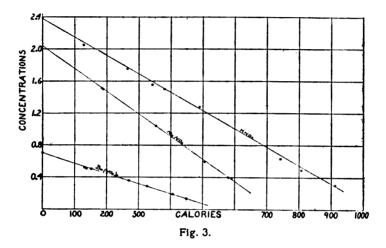
Potassium Nitrate.

The last three results given in this series of readings were obtained

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in the last column are of course interpolated from the other results. This not only tends to show that the results are free from instrumental errors but that the break in the curve of potassium chloride is due to some chemical change taking place in the solution. It is probable that other substances would show this same effect if greater differences of concentration had been used.

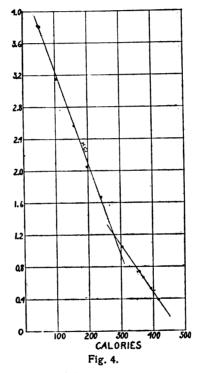


The results are represented graphically in Figs. 3 and 4. The ordinates show the concentrations, and the abscissa the total heat absorbed when that quantity of solution containing one mol was diluted from the highest concentration (that represented by the intercept of the curve on the ordinate axis) to the concentration in question.

Conclusions. — It is evident from these results that the value of dU/dc is a constant within the limits of concentration here shown if we represent by U the heat in calories per gram-molecular weight and by c the concentration of weight normal solutions. This corresponds to the fact that as the concentration approaches zero the heat effect produced by the addition of a definite amount of solvent dv to the solution approaches zero.

The fact that  $dU/dv = a/v^2$ , where a is a constant would seem to show that there is a similarity between the heat of dilution of a solution and the Joule-Thomson effect in gases for which as is well known, the same expression holds true. F. L. BISHOP.

This result would indicate that the osmotic pressure P, like the gas pressure in van der Waals's equation, must be corrected by a term  $a/v^2$  representing the attraction of the molecules. The product Pdv would then represent the external work done when the volume of the solution is increased under the osmotic pressure P by the



volume dv and the term  $(a/v^2)dv$  would represent the internal work done in overcoming the attraction, which is equivalent to the heat of dilution.

I take this opportunity to thank Professor A. A. Noyes for placing a room and equipment of the Research Laboratory of Physical

# THE RELATION BETWEEN "POTENTIAL TEMPERA-TURE" AND "ENTROPY."<sup>1</sup>

#### BY L. A. BAUER.

IN 1888 the late Professor von Helmholtz incidentally introduced the term "waermegehalt" in connection with his investigations,<sup>2</sup> "On Atmospheric Motions." According to him the "waermegehalt" or the actual heat contained in a given mass of air is to be measured by the absolute temperature which the mass would assume if it were brought adiabatically to the normal or standard pressure. It remained for the late Professor von Bezold, however, to perceive the full significance of this term and to reveal its important bearing in the discussion of meteorological phenomena.

As the quantity really involved in this new term is not a quantity of heat, von Bezold suggested that the term be replaced by the evidently more appropriate one of "potential temperature."<sup>3</sup> This met with von Helmholtz's approval.

With the aid of this happy idea of "potential temperature" von Bezold was enabled to draw in a simple and beautiful manner a number of important conclusions governing thermodynamic phenomena taking place in the atmosphere. Thus, for example, he found that :

"Strict adiabatic changes of state in the atmosphere leave the potential temperature unchanged, whereas pseudo-adiabatic ones invariably increase the same, the increase being in proportion to the amount of aqueous evaporation."

Von Bezold called attention to the fact that this law bears a strik-

<sup>3</sup> Sitzb. Berliner Akad., 1888, V. XLVI., p. 1189, "Zur Thermodynamik der Atmosphaere"; also in von Bezold's "Gesammelte Abhandlungen," Vieweg und Sohn, Braunschweig, 1906, p. 128. A translation will be found in Abbe's Mechanics, etc., p. 243.

<sup>&</sup>lt;sup>1</sup> Presented before the Philosophical Society of Washington, March 16, 1907.

<sup>&</sup>lt;sup>4</sup> Sitzungsberichte Berliner Akademie, 1888, V. XLVI., p. 652, "Ueber atmospherische Bewegungen," see translation in Abbe's Mechanics of the Earth's Atmosphere, Washington, 1891, p. 83. The symbol  $\theta$  is used to denote the "Waermegehalt."

ing resemblance to the well-known theorem of Clausius, now commonly known as the second law of thermodynamics, viz. : "that the entropy strives towards a maximum;" but, he says, "it is not identical with it."

The purpose of this paper is to examine into the precise relationship between the two functions "potential temperature" and "entropy" and to see whether any use could be made advantageously of the former in the treatment of certain thermodynamic problems as well as to ascertain wherein the potential temperature law fails to give full expression of the second law of thermodynamics. To my knowledge no application has as yet been made of the new term in treatises on thermodynamics. The substance of this paper was communicated to the American Association for the Advancement of Science at the Springfield meeting in 1895, but publication pending opportunity for further elaboration was deferred.

The "potential temperature" of a body is defined as the absolute temperature assumed when the body is brought adiabatically to standard pressure.

Defining the thermodynamic state per unit of mass of a body by the three variables, T, the absolute temperature, v, the volume per unit of mass, p, the pressure supposed uniform, the following characteristic equation subsists between them : T = f(v, p).

If the body be brought now adiabatically to standard pressure  $p_0$ , then the temperature assumed at the end of the process is the so-called *potential temperature* as above defined and is designated by the symbol  $\theta$ . Hence,

$$\theta = f(v, p_0). \tag{1}$$

For a perfect gas, since kT = pv, k being a constant for any particular gas,

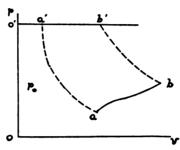
$$\theta = \frac{\dot{p}_0}{k} \cdot v = k_0 \cdot v, \qquad (2)$$

or the potential temperature for any particular gas is directly proportional to the volume and, hence, as von Bezold showed, the potential

Hence, were it possible to express the entropy function for perfect gases directly in terms of potential temperature, we should likewise have for certain cases an easy graphical representation of the entropy function.

In the pv diagram opposite let aa' and bb' represent portions of two adiabats, and o'a'b' be the line of standard pressure  $p = p_0$ .

Suppose the initial thermodynamic state of the body experimented upon be represented by the point *a* and some process ab be carried out. According to definition, the potential temperature,  $\theta_a$ , in the state *a* will be the temperature at the point along the adiabat aa' where it is intersected by the



line of standard pressure. But according to equation (2) the temperature at, this point, a', is proportional to the volume, *i. e.*, to o'a'. Similarly the potential temperature in the state b will be proportional to the abscissa o'b'. Hence if measured on the same scale, o'a'and o'b' will represent directly for the same substance the respective potential temperatures. It is thus easy to represent graphically at any stage of the process ab the corresponding potential temperature.

If it is desired to determine the numerical value of the potential temperature, this can be done with the aid of the equation of the adiabat thus:

 $\theta_a = \theta_{a'} = T_a \left( \frac{v_a}{v_a} \right)^{\epsilon-1} = T_a \left( \frac{p_0}{p} \right)^{\epsilon-1},$ 

or

$$\theta_{a} = \left(\frac{p_{0}v_{a}}{k}\right)^{\epsilon} T_{a}^{\frac{1}{\epsilon}} = k'v_{a}^{\frac{\epsilon-1}{\epsilon}} T_{a}^{\frac{1}{\epsilon}}.$$
(3)
$$[\epsilon = 1.41].$$

For a perfect gas, the entropy, s, per, unit of mass may be expressed by the following equation:<sup>1</sup>

$$s = \int -\frac{dh}{T} = c_r \log T + k \log v + \text{const.}, \qquad (4)$$

<sup>1</sup>See, e. g., Planck's Thermodynamics.

 $c_p$  and  $c_s$  are, respectively, the specific heats at constant pressure and at constant volume; k is a constant for any particular gas. Utilizing equation (3) and remembering that

 $\epsilon = \frac{c_p}{c_s}$  and  $k = (c_p - c_r)$ 

we get

or

$$s = c_p \log \theta + (\varepsilon - 1) \log \frac{k}{p_0} + \text{const.},$$
$$s = c_p \log \theta + \text{const.}$$
(5)

This gives us the relation sought between potential temperature and entropy. Since  $c_p$  is invariably a positive quantity, it follows at once that for any process the potential temperature varies in precisely the same direction as the entropy. If the entropy is increased, as it invariably is for irreversible processes in accordance with the second law of thermodynamics, then is the potential temperature likewise increased. When the entropy remains constant, as for reversible processes, *e. g.*, a strict adiabatic process, then the potential temperature likewise remains constant. In other words as far as perfect gases are concerned it is possible to express the entropy function in its simplest form by means of a quantity — the potential temperature — not only readily interpretable but also easy of direct graphical representation.

Owing to the intimate relationship between entropy and potential temperature the term "entropic temperature" might appear as being possibly a more suggestive one for von Helmholtz's "waermegehalt" than that of "potential temperature," but it may hardly seem advisable now since von Bezold's extensive use of the latter term to recommend a change.

Cyclical Process. — By turning back to the diagram, it will be seen that the change in potential temperature in going from a to bis precisely the same as from a' to b', *i. e.*, the same as for a simple expansion process under constant pressure. Hence, in carrying out the cyclical process abb'a'a, it will readily be seen that the sum total of the potential temperature changes is zero, just as in the case of the sum total of the entropy changes. We have in general:

$$s_b - s_a = c_p(\log \theta_b - \log \theta_a) = c_p(\log \theta_{b'} - \log \theta_{a'}), \qquad (6)$$

or the entropy change in passing from a to b by any process whatsoever — reversible or irreversible — can be measured ideally by the temperature changes incurred in allowing the body to expand under standard pressure between the initial and final adiabats.

For other Substances. — If the substance acted upon be not a perfect gas we have :

$$\int_{a}^{b} ds = s_{b} - s_{a} = \int_{a'}^{b'} - \frac{dh}{T} = \int_{a'}^{b'} c_{p} \frac{d\theta}{\theta} = \int_{a}^{b} c_{p} \frac{d\theta}{\theta}.$$
 (7)

Here  $c_p$  is not a constant as in the case of a perfect gas, but varies with temperature and may even be discontinuous, hence it is impossible, in general, to carry out the integration of the right-hand member. This we know, however, that  $c_p$  is invariably positive, *i. e.*, heat must always be *supplied* to a substance to raise its temperature under a constant pressure. Since

$$ds = c_p \frac{d\theta}{\theta}, \qquad (8)$$

it follows that the sign of ds is the same as that of  $d\theta$ , so that whenever the entropy increases, the potential temperature does likewise. This, while true for cases treated, is not so, in general, as previously explained.

In the foregoing paragraphs the law of potential temperature has been deduced from that of entropy, however, an independent deduction can readily be made if desired.

For example, we may build up the law of potential temperature in precisely the same manner as in the case of the entropy law by taking typical examples of natural processes and showing that nature unaided invariably tends to increase the potential temperature.

Thus take the well-known case of the sudden expansion of a perfect gas without the performance of external work. It is very So again with the case of heat conduction. Suppose we have the same mass of the same perfect gas enclosed in each of two vessels a and b of the same size and enclosed in a non-conducting vessel. The temperature of a is greater than b. Connect now aand b thermally whereupon in accordance with nature's law heat will flow from the hotter body to the colder until the two are of the same temperature. It will be found that here again the potential temperature of the entire system at the end of the process is greater than at the beginning. This may be proven most readily thus : For a perfect gas we have from (3), when the volume remains constant :

hence

$$d\theta = \frac{k''}{\varepsilon} \cdot \frac{\mathbf{I}}{T^{\mu}} d\mathcal{I},$$

 $\theta = k'' T^{1/\epsilon}.$ 

where  $\mu = I - I/\epsilon$  = positive quantity, since  $I/\epsilon < I$ . Consequently, the change in potential temperature for a given change in absolute temperature, the volume remaining constant, decreases with absolute temperature. Hence, although the two bodies, a and b, under the conditions imposed, change in absolute temperature by the same amount, the first losing, the second gaining, because of the law just stated, the potential temperature of the colder body, b, suffers a greater increase that the decrease in potential temperature experienced by the warmer body, a, which was to be proven.

So also for imperfect gases the law of increase of potential temperature for natural processes can be established independently of the entropy principle. It is merely necessary to show that in general the adiabat is steeper than the isotherm or that the change in potential temperature varies inversely with the absolute temperature, when the volume remains constant.

Thus far it has appeared as though the potential temperature law might suffice equally as well as the entropy law. However, in

the latter. Equation (8) shows likewise that the substitution of the obviously more convenient function — potential temperature for entropy cannot be made in general. There are doubtless, however, a number of thermodynamic problems as was shown by von Bezold, as also in this paper, where the application of the potential temperature law may be found convenient. The main purpose of this paper, as above stated, has been to show the precise relationship between the two functions.



#### PROCEEDINGS

#### OF THE

# American Physical Society.

#### MINUTES OF THE THIRTY-NINTH MEETING.

THE annual meeting of the Physical Society was held in the Ryerson Physical Laboratory of the University of Chicago during the week beginning Monday, December 30, 1907. The meeting was a joint meeting with Section B of the American Association for the Advancement of Science. Sessions for the presentation of papers were held on December 30, 31, 1907, and January 1, 2, 1908.

The annual business meeting of the Society was held on Wednesday, January 1, 1908.

Tellers being duly appointed the ballots for the annual election were counted and the following gentlemen were declared elected as officers of the Society for the year 1908:

President. - E. L. Nichols.

Vice-President. --- Henry Crew.

Secretary. - Ernest Merritt.

Treasurer. - J. S. Ames.

Members of the Council. - W. C. Sabine and S. W. Stratton.

The Council brought before the meeting a request from the College Entrance Examination Board that the Physical Society coöperate with it in the formation of a Commission to consider the revision of the definition of the Board's present entrance requirement in Physics.

After discussion it was moved, and carried by a large majority, that the invitation be declined on the ground that the teaching of Physics and all pedagogical matters lie outside the province of the American Physical Society.

The following papers were presented :

1. Note on Spark Potentials. R. F. EARHART.

5. Radioactivity of a Smoke-laden Atmosphere. S. J. ALLEN.

6. On the Value of the Charges Carried by the Negative Ion of Ionized Gases. R. A. MILLIKAN and L. BEGEMAN.

7. The Distribution of Ionizing Energy about an X-ray Tube in Action. W. R. HAM.

8. The Velocity of the Negative Ions Produced by the Ultra-violet Rays. ALOIS F.  $Kov A^{R}IK$ .

9. The Variation of Apparent Capacity of a Condenser with the Time of Discharge and the Variation of the Capacity with Frequency in Alternating Current Measurements. BRUCE V. HILL.

10. The Capacity of Paper Condensers and Telephone Cables. An-THONY ZELENY and A. P. ANDREWS.

11. An Examination of Certain Alternating Current Circuits, Including those Containing Distributed Capacity. CARL KINSLEY.

12. A Comparison of the Formulas of Helmholtz and Nernst for the Electromotive Force of Concentration Cells. HENRY S. CARHART.

13. Determination of the Fusion Points of Sodium Nitrate and Potassium Nitrate. FLOYD R. WATSON.

14. The Stability of Cadmium Cells. HENRY S. CARHART.

15. On the Separation of Echelon Spectra by Gratings. A. A. MICHELSON.

16. Upon the Magnetic Separation of the Spectral Lines of Barium, Yttrium, Zirconium and Osmium. B. E. MOORE.

17. Heat of Evaporation of Water. A. W. SMITH.

18. A Satisfactory Form of High Resistance. G. W. STEWART.

19. A New Apparatus for Measuring Electrolytic Resistance. ARTHUR W. SMITH.

20. The Resistance Temperature Coefficient and the Coefficient of Expansion of Carbon. G. W. STEWART.

21. The Temperature Coefficient of the Moving Coil Galvanometer. A. ZELENY and O. HOVDA.

22. The Use of Complex Quantities in Alternating Currents. G. W. PATTERSON.

23. Physical Research at a Mountain Observatory. George E. HALE.

24. Some Cases of Excessive Damping of Torsional Vibrations. K. E. GUTHE.

25. The Effect of Tension on Thermal and Electrical Conductivity. N. F. SMITH.

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29. The Distribution of Energy in the Spectrum of the Tungsten Filament. (Read by title.) R. E. NYSWANDER.

30. The Infra-red Absorption of Certain Biaxial Crystals for the Three Principal Directions of Vibration. R. E. NYSWANDER.

31. Ionization of Gases at High Pressures. HENRY A. ERIKSON.

32. The Susceptibility of Copper and Tin and their Alloys. O. C. CLIFFORD.

33. The Magnetic Properties of Antimony. ARTHUR L. FOLEY.

34. A Galvanometer Scale for the Direct Reading of Temperatures with Thermo-electric Couples. ANTHONY ZELENY.

35. The Heat of Dilution of Aqueous Salt Solutions. F. L. BISHOP.

36. How does a Violinist Control the Loudness of his Tone? HARVEY N. DAVIS.

37. A Repetition of the Wheaton Experiment of 1834. FRANCIS E. NIPHER.

38. Some Curious High Temperature Phenomena. C. E. MEN-DENHALL.

39. On the Variations in the Penetrating Radiation from the Earth. C. S. WRIGHT.

40. On the Radioactivity of Potassium Salts. J. C. MCLENNAN.

41. On the Absorption of Short Electric Waves by Air at Different Pressures. J. E. Ives and R. E. C. Gowdy.

42. A Hydrogen Peroxide Cell. (Read by title.) H. T. BARNES and G. W. SHEARER.

43. The Spectrum of Calcium. (Read by title.) JAMES P. BARNES.

44. Selective Reflection as a Function of the Atomic Weight of the Base. (Read by title.) W. W. COBLENTZ.

45. A Wave Machine Showing Damped or Undamped Compound Waves. (Read by title.) ALBERT B. PORTER.

46. Notes on Harmonic Analysis. (Read by title.) ALBERT B. PORTER.

47. A Mechanical Effect Accompanying Magnetization. (Read by title.) O. W. RICHARDSON.

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49. Absorption Spectra of Roentgen Rays measured by a Radiometer. (Read by title.) J. M. ADAMS.

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# An Investigation of the Electric Displacement and Intensities Produced in Insulators by Their Motion in a Magnetic Field, and its Bearing on the Question of the Relative Motion of Ether and Matter.<sup>1</sup>

#### BY S. J. BARNETT.

IF a particle with electric charge q moves with velocity v in a magnetic field whose induction is B, it is acted upon by a force

$$F = V v B. \tag{1}$$

Hence in a portion of matter moving in a magnetic field there is, on the theory of Lorentz, according to which matter is built up of electrified constituents and the ether is at rest, an intrinsic electric intensity

$$e = F/q = VvB \tag{2}$$

acting on the matter only, but not on the permeating ether. The resulting displacement of the particles of matter gives rise to an electric field intensity E acting on both matter and ether, the actual electric displacement at any point depending on both intensities and on the dielectric constant of the medium. If the ether moves with the matter, it also is acted upon by the intrinsic intensity VvB, and the resulting displacement will be different. The intensities, displacements, e.m.f.'s, and charges can be calculated without difficulty in certain simple cases suitable for experimental discrimination between the two theories.

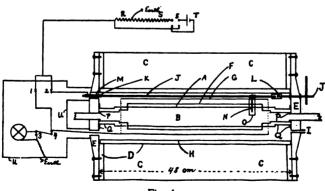


Fig. 1.

cylindrical coil C of copper wire wound on a brass bobbin DD. The magnetic field is produced by a current in this coil. The bearings EE in which the rotor B moves are of lumen screwed to the flanges forming the ends of the bobbin DD. The cylinder A is covered with a thin conducting coat F. A little longer than A, and surrounding it coaxially, is a uniform brass tube G. Surrounding this are the coaxial brass tubes H and D, the latter a part of the bobbin, and both together forming, with the brass rings soldered between them at the ends, a jacket for water or air. The tube G is insulated from H by small blocks of amberoid. Between these tubes is a brass rod *II*, capable of being rotated in the brass bearings K and K near its ends. The rod is cut near its right end and the two parts are separated by a block of amberoid L. At the left end the bearing K is insulated by means of a surrounding amberoid block M. Screwed to the insulated part of the rod JJ is a brass wire N, by which it may be brought into contact with the metal coat F of A without touching the tube G. For this purpose a small slit O is cut in G. Small ebonite rings PP make the electrical contacts between the rotor and the bearings always nearly the same. Brass tubes QQ of very nearly the same diameter near A as that of the part of the rotor within A, and coaxial with A, extend from the bearings almost into contact with B, and form electric screens. Except as shown in the figure, the space within C is practically metal-enclosed. A slow stream of dry dust-free air enters through the tube I. A potentiometer RS and battery T, with commutator 5, produce the voltage (along R) used for standardization purposes. Amberoid keys 1, 2, 3, 4, of special design, connect G and J with the battery and an electrometer, all connections being made within the brass case U, which is earthed. The rotor is driven at various speeds by an electric motor.

The observations, aside from those involved in preliminary experiments and in the determination of certain constants, consist of two parts, (1) calibration, and (2) experiment proper. In (1), keys 1, 2, 3 are initially closed, N is down, or in contact with F, and 4 and 5 are open. Then, in succession, 5 is closed, N is raised, 5 is opened, 1 is opened, 4 is closed, 3 is opened, N is lowered, and the electrometer scale reading is taken. The process is repeated with 5 reversed. The double deflection  $d_0$  corresponding to the voltage  $V_0$  along R is determined. In (2), keys 1 and 5 are initially open, 2, 3, 4 closed, N down, the rotor at rest, the current in the coil zero. Then, in succession, N is raised, the motor is started, the coil circuit is closed, the current is determined, 3 is opened, the coil circuit is broken, the motor is stopped, N is lowered, and the electrometer scale reading is taken. The process is repeated with the current in the coil reversed. The double deflection d corresponding to the coil current I and the period T of the rotor (recorded



by a chronograph) is thus found. All the operations are so timed as to eliminate as many errors as possible.

If now K denotes the dielectric constant of the medium under investigation,  $\varphi$  the mean magnetic flux per unit current in the coil across a right section of the hollow cylinder A,  $\varphi'$  the mean flux per unit current in the coil across a right section of the metal cylinder F, and V the mean voltage from the surface of the part of the rotor within A to the earth, it follows from Lorentz's theory as developed for the above experiment that

$$\frac{d}{d_0}V_0 = \left(\varphi \frac{K-1}{K} + \varphi' + V\right) \frac{I}{T}$$
(3)

or

$$\frac{Td}{I \,\overline{d}_0} V_0 - (\varphi' + V) = \varphi \frac{K - 1}{K}$$
(4)

suitable units being used. If the ether moves with the matter, unity must be substituted for (K-1)/K.

Two series of experiments have been completed, one with a cylinder of sulphur, the other with a cylinder of rosin. In each case  $\frac{d}{d_0}V_0$  was found to be proportional to I/T as required by either (3) or the corresponding equation for the ether-motion theory.

In the case of sulphur the mean value of

$$\frac{T}{I}\frac{d}{d_0}V_0 - (\varphi' + V)$$

was 0.0<sup>4</sup>1077, while  $\varphi$  and  $\varphi \frac{K-1}{K}$  were respectively 0.0<sup>4</sup>1450 and 0.0<sup>4</sup>1077, equation (4) being thus confined within a fraction of 1 per cent. This closeness of agreement is to some extent accidental, as the observations differed much more widely among themselves.

In the case of rosin, the mean value of

$$\frac{T}{I}\frac{d}{d_0}V_0 - (\varphi' + V)$$

was 0.0<sup>5</sup>792, while  $\varphi$  and  $\varphi \frac{K-1}{K}$  were respectively 0.0<sup>4</sup>1308 and 0.0<sup>5</sup>870, the theory of Lorentz being again confirmed, though not so closely as before.

Further experiments, on different insulators and with improved conditions, are in progress.

In an investigation on this subject begun later than this one, but published in 1904,<sup>1</sup> Dr. H. A. Wilson, of Trinity College, Cambridge, gave,

<sup>1</sup> Phil. Trans. Roy. Soc.

with the assistance of Professor Larmor, formulæ for his experiment which are incomplete and incorrect. The correct formula is

$$q_0 \frac{d}{d_0} = \left[ (K - I) S_0 \varphi + S(\varphi' + V + V') + S'V' \right] \frac{I}{T}$$
 (5)

proper units being used. Here  $\varphi$ ,  $\varphi'$ , V, I, T, and K have the same meanings as in (3) and (4);  $S_{a}$  is the capacity the ebonite cylinder would have if ebonite were replaced by ether and the electric field were confined to the region between the coats, and if the lines of intensity were all straight; S is the actual capacity of the ebonite condenser so far as this depends on the tubes of displacement stretching between the outer coat and the inner cylinder; S' is the capacity of the tubes stretching between the outer coat and the case, but does not include the capacity S' of the electrometer, brush, and wires, which do not revolve; V is the mean voltage from the insulated electrometer quadrant and brush to the outer surface of the outer coat of the ebonite;  $d_0$  is the electrometer deflection when the outer coat and connections have the charge  $q_0$ ; and d is the electrometer deflection produced when the ebonite revolves in the magnetic field. Instead of  $S_0$ , Wilson has what he considered the actual capacity the condenser would have with air substituted for ebonite, so far as tubes of displacement stretching between the outer coat and the inner one are concerned; for S', he has S + S', neither of which was determined separately. Hence it is impossible to say what is the discrepancy between his results and those called for by the theory of Lorentz. Attention has already been called ' to another error in Wilson's theory, which, however, did not affect his experimental work or calculations.

The troublesome terms S' and V' in the above formula, and with them what was perhaps the greatest experimental difficulty with which Wilson met, can both be eliminated by surrounding the rotating cylinder and brush with a second cylinder also connected with the electrometer or brush by a wire at rest.

ON THE EMISSIVITY OF MOLTEN IRON AND COPPER.<sup>3</sup>

#### BY CHARLES B. THWING.

N UMEROUS attempts made by the writer and others, to measure the temperature of molten iron with the Féry radiation pyrometer led invariably to results which were obviously much too low. The pyrometers employed were, in some cases, furnished for the express purpose of measuring the temperature of molten iron yet the reading obtained by

<sup>1</sup>Roy. Soc. Proceedings, 1905.

<sup>2</sup> Read before the American Physical Society, October 19, 1907.



pointing the telescope at the flowing iron was considerably less than that from the same iron as it solidified in a ladle. Similar experiments tried with the writer's radiation pyrometer, which, like that of Féry, makes use of the total radiation from the surface of the metal, led to the obvious conclusion that the emissivity of clean molten iron is much less than that of a black body, which solid iron approaches quite closely.

As no data were available a series of experiments was undertaken to determine, at least roughly, the constant of radiation for iron and copper since the importance of a knowledge of the temperature of these metals in various industrial operations is coming to be recognized by metallurgists as of considerable importance, and the principle of total radiation offers an extremely convenient means of making such measurements.

Apparatus. — The radiation pyrometer employed consists of a receiving tube and a portable galvanometer. The receiving tube is of light steel oxidized to blackness on its inner surface and is 90 cm. long and 25 mm. in diameter. At the front or receiving end, a diaphragm determines the angular aperture in conjunction with a conical mirror placed about 70 cm. distant near the other end of the tube which is held in the hand when the tube is pointed at the surface whose temperature is to be The radiations are received near the apex of the mirror upon measured. a thin couple of iron-constantan which reaches a state of thermal equilibrium in about 2 seconds after exposure to the radiations. Since all radiations reaching the mirror are transmitted by multiple reflection to the surface of the couple regardless of their direction the instrument is in focus for all distances. The angular aperture being constant the indications are independent of the distance of the object so long as the surface is larger than is required to fill the angle.

The galvanometer is of the pivoted type and therefore does not require leveling, thus making rapid work possible in situations where the time required for setting up and focusing a telescope and leveling the galvanometer would be a decided hindrance. The instrument is compensated for temperature variations in the resistance of the moving coil by an automatic variation of the magnetic reluctance. This arrangement makes unnecessary the introduction of a dead resistance for swamping the variations due to temperature and permits good control of the needle by the control spring with a fairly high sensibility. Three millivolts is sufficient to produce a full scale deflection of 60 degrees. The scale is calibrated by the Stefan-Boltzmann law,  $d = K(T^4 - T_a^4)$ .

Direct measurement of the temperature of the iron was made by means of two Le Chatelier pyrometers by Keiser & Schmidt. The couples were enclosed in quartz tubes and, in some cases, further protected by iron or graphite tubes. The short life of the couples precluded the taking of a large number of observations by their means. Method of Observation. — At the iron foundry the iron was drawn continuously from the cupola into a large mixing ladle whence it flowed under a dam into the pouring ladles. The receiving tube was pointed alternately at the stream flowing into and out of the mixing ladle while the Le Chatelier couple was immersed in the ladle, the temperature measured by the couple being considered the same as the average temperature of the two streams. The fall of temperature in the ladle was about 40 degrees.

At the Bessemer plant the Le Chatelier couple was inserted in the fifteen-ton pouring ladle and the radiation measured from the stream as it issued from the botton of the ladle. The stream was here certainly free from all slag and oxide. A similar condition was quite fully realized at the iron foundry by pointing at the lower or back side of the stream.

*Results.* — For cast iron at  $1,300^{\circ}$  to  $1,400^{\circ}$  C. the intensity of total radiation from the molten metal was found to be 0.29, and for mild steel at  $1,600^{\circ}$  to  $1,650^{\circ}$  C., 0.28, that of the radiation from solid metal at the same temperatures.

Observations made upon open-hearth furnaces within the furnace, where black body conditions obtain, and at the stream as it issues from the furnace, indicate that the value found holds for temperatures up to  $1,800^{\circ}$ .

A smaller number of observations made upon copper gave a value for the emissivity of that metal in the molten state of but half that of iron or 0.14 that of a black body. The low emissivity of molten copper has been remarked by workmen, who find that molten copper in the ladle burns the face much less than the same copper when cooling in large ingots where the exposed surface is about the same as in the ladle.

Large numbers of measurements of molten iron give concordant results and point to a constancy of the constant for molten metal sufficient to permit of the use of the same pyrometers as are used for solid metals by the use of a factor or by employing two scales.

#### HEAT OF EVAPORATION OF WATER.

#### By ARTHUR WHITMORE SMITH.

THE heat of evaporation of water is one of the important constants of nature. It has far-reaching practical applications, especially at high temperatures, while at low temperatures it enters into many problems of the physicist, the chemist and the meteorologist. Unfortunately few determinations have been made at ordinary temperatures, and my

<sup>1</sup>Abstract of a paper presented at the Chicago meeting of the Physical Society, December 30, 1907, to January 2, 1908.



recent work <sup>1</sup> was undertaken to fill this gap. The method employed was to draw a stream of dry air through water within a calorimeter and determine the amount of water evaporated by again drying the air and weighing the water thus collected. Heat to maintain a constant temperature was supplied by an electric current and the results are expressed in terms of international joules per gram of water evaporated.

The present paper <sup>3</sup> gives the final corrected results expressed in terms of "mean calories" as well as in joules. The true value of the E.M.F. of a Clark cell at 15° C. is much nearer 1.433 volts than the legal and accepted value, 1.434 volts. It is further shown that the most applicable value of J is that determined by Reynolds and Moorby and corroborated by Barnes, viz., 4.1834 joules per mean calorie. Using these factors and the weight of water corrected for the buoyancy of the air gives the following values :

Temperature Centigrade.	Heat of Joules.	Evaporation. Mean Calories.	
13.95	2462.5	588.6	
21.17	2446.1	584.7	
28.06	2430.2	580.9	
39.80	2401.0	573.9	

Plotting these values on a sheet of accurately engraved cross-section paper, together with all the results of other investigations at both higher and lower temperatures, gives a concordant curve from  $0^{\circ}$  C. to  $100^{\circ}$  C. The agreement is especially good for the range  $0^{\circ}$  C. to  $50^{\circ}$  C., while the uncertainty at  $100^{\circ}$  C. is probably not over 0.2 per cent.

From this curve are obtained the following values, which represent our best knowledge of the subject at the present time:

Temperature Centigrade.	Mean Calories.	Temperature Centigrade.	Mean Calories.	Temperature Centigrade.	Mean Calories.
0	596.3	35	576.9	70	556.3
5	593.6	40	574.0	75	553.3
10	590.9	45	571.1	80	550.3
15	588.1	50	568.2	85	547.3
20	585.3	55	565.3	90	544.3
25	582.5	60	562.3	95	541.2
30	579.7	65	559.3	100	538.0

Heat of Evaporation of Water-0° C to 100° C.

UNIVERSITY OF MICHIGAN, ANN ARBOR. MICH.

# THE TEMPERATURE COEFFICIENT OF THE MOVING COIL GALVANOMETER.<sup>1</sup>

#### BY ANTHONY ZELENY AND O. HOVDA.

THE temperature coefficient of a moving coil galvanometer having a cast-iron magnet, was determined in order that the change in the sensibility could be calculated when the instrument is used at different temperatures.

Since the temperature coefficient depends upon the magnet, the suspensions and the coil, and in different relations for different kinds of measurements, the coefficients of these different parts were determined separately. These are combined in their proper relation to determine the temperature coefficients for current, potential and ballistic measurements.

THE CAPACITY OF PAPER CONDENSERS AND TELEPHONE CABLES.<sup>1</sup>

BY ANTHONY ZELENY AND A. P. ANDREWS.

THE free charge' capacities of various paper condensers and a telephone cable were compared with their capacities as obtained by the ordinary method where the galvanometer remains connected during the whole period of its throw.

The accuracy with which the free charge can be determined is shown by discharge curves which give the relation between the quantity and the time of discharge. In most cases, the free charge determinations can be made to within one tenth of one per cent., and the capacities as obtained by the ordinary method are shown to be from 2 to 300 per cent. greater than the free charge capacities, the amount of difference depending on the condenser.

Errors are shown to exist in the present methods of determining the specific inductive capacities of dielectrics and in the resistance of dielectrics as obtained by the loss of charge method.

PHYSICAL LABORATORY,

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UNIVERSITY OF MINNESOTA.

#### A MECHANICAL EFFECT ACCOMPANYING MAGNETIZATION.<sup>1</sup>

#### BY O. W. RICHARDSON.

O<sup>N</sup> the view that the magnetic properties of bodies are due to the motion of electrons in closed orbits, magnetization is accom-<sup>1</sup>Abstract of a paper presented at the Chicago meeting of the Physical Society, De-

cember 30, 1907, to January 2, 1908.

<sup>a</sup>A. Zeleny, PHYS. REV., 1906, Vol. 22, p. 65.

panied by the acquirement by the revolving electrons of a resultant moment of momentum about the direction of magnetization. The magnitude of this moment of momentum is calculated, and it is shown that in the general case the moment of momentum per unit volume is proportional to the intensity of magnetization. In the case where all the revolving electrons are of the same sign, the coefficient of proportionality reduces to 2m/e where *m* is the mass and *e* the charge of an electron. If, as is generally assumed, the revolving electrons in all real bodies are alike as to mass and charge, this coefficient should be the same for all substances. Experiments are being made at Princeton University to detect the existence of this moment of momentum, which should give rise to effects within the reach of experimental measurement.

NOTES ON SPARK POTENTIALS.<sup>1</sup>

BY R. F. EARHART.

Point and Plane. — Measurements were made on the P.D. required to cause a discharge between a needlepoint and a plane surface, for very small distances.

Potentials were secured from a bank of storage cells. Distances were measured by means of an interferometer.

Curves are shown representing the relation between distance and potential. One family of curves represents discharge from a positive point for pressures of 75 cm., 37 cm. and 25 cm. In a similar manner results obtained for point negative are shown.

The least potential required for ionization of air under these conditions is 338 volts, a value somewhat less than has been previously determined for plane electrodes.

Potentials less than 338 volts can produce a discharge, but of a different character. Such discharge is probably produced by the projection of corpuscles or metal atoms. The polarity of the point does not influence the discharge for the abnormally small distances. For greater distances discharge occurs more readily from a negative than for a positive point.

Discharge Between Metal Electrodes for Potentials Less than Ionizing Potentials. — Hobbs has shown that discharge produced by potentials less than an ionizing potential depends on the character of the metal electrode. Such discharge can be secured through greater distances if Al electrodes are used than if Pt were employed.

Using electrodes of Pt, Al, and Ag, in the various permutations and plotting P.D. and distance, I have found that discharge is not determined

<sup>1</sup>Abstract of a paper presented at the Chicago meeting of the Physical Society, December 30, 1907, to January 2, 1908.

by the character of the negative electrode but rather by the electrode having the lower potential gradient, irrespective of its polarity.

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This indicates that the discharge under these conditions is not carried entirely by negative corpuscles.

# ON THE ABSORPTION OF SHORT ELECTRIC WAVES BY AIR AT DIFFERENT PRESSURES.<sup>1</sup>

BY JAMES E. IVES AND ROBERT E. CLYDE GOWDY.

I T has been known for some time past that wireless telegraph messages can be sent farther at night than in the day. One of the explanations of this fact which have been advanced, is that the sunlight ionizes the air, and that this ionization causes an absorption of part of the energy of an electric wave.

It was suggested by Professor Louis T. More that this problem could be reduced to a laboratory experiment by sending short electric waves through air enclosed in a glass tube at different pressures and under different conditions of ionization, and determining what absorption of the energy of the wave, if any, occurred under these differing conditions.

This experiment has, in part, been carried out by the authors during the past year.

The electric waves were generated by an oscillator of a modified Righi type, consisting of two small cylinders of platinum, each 25 mm. long and 2.5 mm. in diameter, sealed into glass tubes. The spark between them took place in kerosene oil.

The resonator was of the Klemencic type, consisting of two brass cylinders each 31 mm. long and 2.5 mm. in diameter, connected together by a thermo-electric junction made of fine iron and constantan wires. A Duddell thermo-galvanometer was used to detect the thermo-electric current.

Between the oscillator and the resonator was placed a glass tube, 44.5 cm. long and 10 cm. in diameter, having pieces of plate glass sealed upon its ends. This tube was air-tight, and the air in it could be rarefied by means of a Geryk pump. The oscillator and resonator were each about 2 cm. from an end of the tube. Behind each of them was placed a parabolic cylindrical mirror made of zinc.

The electric waves generated by the oscillator thus travelled through

nometer. Any increase in the absorptive power of the air in the tube due to its rarefaction was shown by a decrease in the deflection, and vice versa.

The following results have, thus far, been obtained :

For pressures ranging from atmospheric pressure to about .5 mm. of mercury, there are two pressures which give maxima of absorption and at least one pressure which gives a minimum of absorption. One of the pressures which give maxima of absorption is near the zero of pressure, and the other lies between 40 and 60 cm. of mercury. The pressure of minimum absorption lies between 25 and 35 cm. of mercury. At the pressures which give maxima of absorption the absorption is greater than at atmospheric pressure, while at the pressure of minimum absorption the absorption is less than at atmospheric pressure. Near the zero of pressure the absorption decreases rapidly.

The percentage absorption, namely the ratio of the energy absorbed at any pressure to that transmitted at atmospheric pressure, expressed in per cent., is a small quantity, varying between + 7 per cent. and - 7per cent. for the whole tube. This gives a percentage absorption per centimeter of length of the tube varying between + .15 per cent. and - .15 per cent.

UNIVERSITY OF CINCINNATI, December 3, 1907.

# ON THE CHARGE CARRIED BY THE NEGATIVE ION OF AN IONIZED GAS.<sup>1</sup>

BY R. A. MILLIKAN AND L. BEGEMAN.

THE paper is a discussion of the sources of error in preceding determinations of c, and a description of attempts to eliminate some of these sources of error. In its essentials the method employed was that used by H. A. Wilson. The source of ionization was radium. The potential difference established between plates 5 mm. apart in the cloud chamber ranged from 1,600 to 3,000 volts. The expansion was of such value as to cause the fall in pressure to be between 22 and 24 cm. of mercury, its initial value being about 75 cm. The cloud was timed as it fell between the cross hairs of a short focus micrometer telescope, so set that the distance between these cross hairs corresponded to an actual fall of 2 mm. The degree of accuracy with which results could be duplicated may be judged from the following typical set of observations.

<sup>1</sup>Abstract of a paper presented at the Chicago meeting of the Physical Society, December 30, 1907, to January 2, 1908.

	ld 2950 Volts. Field off. ime of fall.	Distance between Plates 5 mm. Field on. Time of fall.
	5.2 sec.	<b>3.8</b> sec.
	4.8 ''	3.8 "
	4.8 ''	3.6 "
	5.2 "	4.0 ''
	5.6 ''	4.0 "
	5.6 ''	4.0 ''
	4.8 "	3.2 "
	5.2 ''	4.0 ''
	5.2 ''	4.0 "
	5.2 "	3.6 "
	5.2 ''	3.6 ''
	5.2 "	3.6 ''
Mean	5.17 sec.	3.77 sec.

Value of e,  $4.25 \times 10^{-10}$  E.S. units.

The results of ten different sets of observations made with fields of the indicated strengths were as follows :

Field Strength.			•	
1600	volts	10.67	E.S.	3.81 × 10-10
2100	"	14.00	"	3.89 "
2400	"	16.00	**	4.10 "
2950	"	19.67	"	4.25 ''
1600	"	10.67	"	4.34 ''
1600	"	10.67		3.66 ''
2100	**	14.00	"	4.10 ''
2250	"	15.00	"	3.94 ''
2350	"	15.67	**	4.37 ''
2750	"	18.30	<i>c6</i>	3.84 ''
	Me	an		$\overline{4.03 imes10^{-10}}$

DETERMINATION OF THE FUSION POINTS OF SODIUM NITRATE AND POTASSIUM NITRATE.<sup>1</sup>

BY FLOYD R. WATSON.

THE object of the investigation is to determine a series of definite melting points of salts from 300° to 1,400° Centigrade that will be helpful in the calibration of thermo-elements and resistance ther mometers.

The determination of the fusion points of the nitrates of sodium and



The salts were melted in a hard glass tube which was surrounded first by a small air space, then by a hot bath of mixed salts. The heating was effected by gas flame and electric current. Temperatures were found by means of a copper constantan thermo-element; the E.M.F. of the latter being determined by a potentiometer. Readings of E.M.F. were taken to microvolts by having the bridge wire of the potentiometer ten meters long, and by arranging the bridge resistance to be only a small part of that of the potentiometer circuit. A certificated cadmium cell was used as a standard E.M.F. The thermo-element was calibrated for ice, steam, and boiling naphthalin and sulphur points.

Results of a number of preliminary observations give the temperature of fusion of sodium nitrate as 307.8° Centigrade, and of potassium nitrate as 336°. Apparatus is now being constructed that will allow these results to be verified with a platinum platinum-rhodium thermo-element, and which will also furnish a means of determining fusion points of salts that melt at higher temperatures.

#### IONIZATION OF GASES AT HIGH PRESSURES.<sup>1</sup>

#### BY HENRY A. ERIKSON.

THIS paper gives the results of an experimental investigation of the ionization produced in gases at high pressures by the  $\gamma$  rays of radium.

The results show that the current obtained with a constant difference of potential between the electrodes becomes a maximum at a certain pressure and that a further increase in the pressure causes a decrease in the current.

The position of the maximum point depends upon the difference of potential. When the potential difference is 18 volts between concentric cylindrical electrodes separated by about 6 mm., the maximum is at a pressure of 70 atmospheres, and the current at 400 atmospheres is 60 per cent. of the maximum. With a difference of potential of 1,000 volts the maximum is at 150 atmospheres, the current at 400 atmospheres being about 78 per cent. of the maximum.

The results also show that some of the ions remain uncombined for some time after the rays have been discontinued. At the end of an interval of 20 seconds the number of ions obtained from air at 200 atmospheres, with a difference of potential of 1,000 volts, is about 8 per cent. of the number obtained at the end of an interval of 0.1 second, and at 400 atmospheres the number is about 13 per cent. for the same intervals.

<sup>1</sup>Abstract of a paper presented at the Chicago meeting of the Physical Society, December 30, 1907, to January 2, 1908. The current-pressure curves for carbon dioxid are approximately similar to those for air, up to the pressure at which the gas liquefies.

Physical Laboratory, University of Minnesota, Dec. 7, 1907.

DISTRIBUTION OF IONIZING ENERGY ABOUT X-RAY TUBES.<sup>1</sup>

BY WM. R. HAM.

THE distribution of ionizing energy about X-ray tubes was examined by an electroscope method in order to detetmine whether the uniformity in distribution obtained by previous observers by photographic and fluoroscopic methods would be found to hold.

Working at one and one half meters distance from the center of the tube there was found to be a wide variation in ionizing energy in certain planes. Thus:

1. In the plane determined by the axis of the cathode and the normal to the target there are large variations, the energy along the normal being about one half as great at a point  $60^{\circ}$  from the normal, where it is a maximum.

2. In the plane at right angles to the preceding plane and containing the normal to the target there are also variations as shown by a large number of curves that cannot be inserted here.

THE EFFECT OF TENSION ON THERMAL AND ELECTRICAL<sup>1</sup> CONDUCTIVITY.

By N. F. Smith.

Two metal bars called A and B of the same material, each  $\frac{5}{16}$  of an inch in diameter and about one meter long are mounted horizontally about 10 cm. apart. One end of each bar is held in a clutch made from a heavy block of copper which is heated and maintained at a constant temperature. By means of thermo-electric couples sliding on the bars a point is determined on B which has the same temperature as a given point on A when the steady state is reached. B is then subjected to a stretching force while the condition of A remains unchanged. When the steady state is again reached the couple on B is shifted till it is again at a point where the temperature is the same as at the given

conductivity is proportional to the square of the length to the position of the thermo-electric couple. At each step the electrical resistances of the two bars are compared by a modification of Kelvin's double bridge method.

Observations have been made on bars of several different metals and each shows an *increase* in the thermal conductivity with the stretching force. The maximum increase is about 1.7 per cent. At the same time the electrical conductivity *diminishes*, the variation being about the same as that found by other experimenters. The length of time that the stress is applied has a marked effect upon the thermal conductivity.

It is proposed to extend the investigation to torsional and bending forces.

Some Cases of Excessive Damping of Torsional Vibrations.<sup>1</sup>

#### BY K. E. GUTHE.

 $D^{ECREASE}$  of the logarithmic decrement with the amplitude, frequently observed in torsional vibrations, is usually extremely small. It is considered as closely connected with the elastic after-effect. Wires of platinum-iridium which are practically free from such after-effect have not alone a large logarithmic decrement but show also a decided decrease of decrement as well as of period with decreasing amplitude. This is especially pronounced in a 40 per cent. platinum-iridium wire whose logarithmic decrement decreased from 0.0137 to 0.0025, while the amplitudes decreased from 5.7 to 0.85 degrees. The corresponding change in the period was from 7.350 to 7.175 seconds. The decrease in amplitude is nearly proportional to the square of the amplitude. With different moments of inertia suspended from the wire the values of the decrement remained the same for the same amplitudes.

Similar effects, though less pronounced, were observed with wires containing a smaller percentage of iridium and in drawn wires of other materials. It was attempted to explain the phenomena by the assumption that the disappearance of the elastic after-effect is very rapid.

The increase of the logarithmic decrement upon drawing was explained by Beilby's theory of the effect of mechanical hardening. A carbon filament was shown to have a large decrement; the electrolytic deposition of hydrogen upon palladium increased the logarithmic decrement

# Absorption Spectra of Röntgen Rays, Measured by a Radiomicrometer.<sup>1</sup>

#### BY J. M. ADAMS.

T has previously been shown photographically<sup>2</sup> that the Röntgen rays from an ordinary focus tube are heterogeneous, that metals show selective absorption toward the different kinds of rays, and that this selective absorption follows different laws with the various metals. The spectrum used in the present paper was obtained by the same method that was used in making the photographs above mentioned, and narrow slits taken from different parts of the spectrum were examined by the radiomicrometer.<sup>3</sup> It was usually found that the beam proceeding from any one of these slits consisted chiefly of rays of one kind, upon which was superposed a small quantity of rays of other kinds. The latter rays were easily removed from the beam by transmission through a metallic sheet of proper thickness, and the beam thus purified satisfied a test for homogeneity, in that its quality, judged by its penetrating power for various substances, was not changed by further transmission through metallic sheets. A beam of rays direct from an ordinary focus tube, on the contrary, shows a decided change of quality after each transmission.

Absorption spectra for metallic sheets of different materials and thicknesses were obtained by placing the radiomicrometer in various regions of the spectrum, and plotting its deflections, reduced by the interposition of the metallic sheet, as ordinates against the distance from one end of the spectrum as abscissa. The resulting curves in some cases were practically straight lines, indicating by their slope that the rays produced by the swiftest cathode particles had the greatest penetrating power'; while in other cases there were well marked maxima and minima of absorption in going along the spectrum.

# A WAVE MACHINE SHOWING DAMPED OR UNDAMPED COMPOUND WAVES.<sup>1</sup>

#### BY ALBERT B. PORTER.

THIS machine compounds two harmonic waves either or both of



thus serves not only to illustrate the ordinary problems in simple harmonic motion, but also the effects of damping by frictional or other resistance, and the phenomena of resonance. It may, for example, be made to portray the effects of resonance in electric circuits, or the decay of speech-currents in telephone cables. The machine simultaneously draws the two component waves, the compound wave, the two circles (or, in the case of damping or resonance, spirals) of reference, and the Lissajous figure which represents the combination of the two harmonic motions.

The machine offers nine choices of ratio of periods between the two simple waves, and each of these ratios may be thrown slightly "out of tune" for the purpose of showing beats, or the changes in the compound wave and the evolutions of the Lissajous figure as the phase progressively changes. There are three choices of wave-length of the fundamental wave. The amplitude of either wave may be given any value between zero and the maximum permitted by the size of the machine; the phase difference can be varied between  $0^\circ$  and  $360^\circ$ ; and either wave may be given any desired positive or negative damping coefficient.

#### NOTES ON HARMONIC ANALYSIS.<sup>1</sup>

#### BY ALBERT B. PORTER.

THIS paper describes: (1) A geometrical representation of the Fourier coefficients of a periodic function as a series of solids; (2) the essential mechanism of an integrating harmonic analyzer which is based on this representation; (3) a new method of harmonic analysis by use of specially ruled sine-coördinate paper, on which the given function is plotted, and the Fourier coefficients are determined by measurement with an ordinary planimeter, and (4) a modified form of the Yule analyzer.

# THE USE OF THE BUNSEN ICE CALORIMETER FOR ACCURATE HEAT MEASUREMENTS.<sup>1</sup>

#### BY H. T. BARNES AND FRANKLIN H. DAY.

IN applying the Bunsen ice calorimeter for measurements of the heating effect of some of the radioactive changes an effort was made to eliminate the uncertainty which always appears in the want of steadiness of the reading. It is a well-known fault with this type of instrument, that the readings are never steady, but have always to be cor-

<sup>1</sup>Abstract of a paper presented at the Chicago meeting of the Physical Society, December 30, 1907, to January 2, 1908.

rected for a slow freezing or melting going on inside the instrument. The creep or "gang" may be reduced in several ways: Bunsen, 1871, used air-free water and applied a considerable hydrostatic pressure, and still obtained a constant increase in reading (freezing).

Schuller and Wartha, 1888, used the same apparatus with water not airfree and obtained a continuous decrease in reading (melting). Boys, Mond, Ramsay and Shields found a continuous increase in their instrument and compensated for it by surrounding the bulb with an air jacket, thus balancing the freezing by a continuous melting.

Dieterici used a modified form of the Dewar flask, surrounding the calorimeter with a vacuum jacket and thus considerably reduced the creep.

One of the authors, with Mr. Lucas, previously made an effort to reduce the creep by surrounding the calorimeter with freezing-point mixtures of great purity, such as clean, freshly fallen snow and distilled water, but did not succeed. It occurred to the authors, after trying tap water with and without air, and water from clean blocks of river ice, all without success, that it was better to use distilled water, eliminate so uncertain a quantity as the dissolved air, and add a very small quantity of cane sugar to the water before filling the bulb of the instrument.

After several trials with various strengths, it was found that a solution of cane sugar containing .18 gram to the liter practically did away with the creep when the instrument was immersed in clear, cracked river-ice and tap water. The capillary tube of the instrument had a bore of .0006619 c.c. per millimeter, and the actual change in reading which was obtained was less than 5 mm. in 14 hours, and was constant for over two days. Changing the height of the capillary tube was found to have a small effect on the creep.

The authors strongly recommend to those desiring to use the Bunsen ice calorimeter that the bulb be filled with a solution containing from .15 to .18 gram per liter, and boiled free from air. The solution is so weak that the sugar added cannot be detected by its taste, and the arrangement is the simplest way to reduce an otherwise uncertain and troublesome correction.

A HYDROGEN PEROXIDE CELL.<sup>1</sup>

BY H. T. BARNES AND G. W. SHEARER.



dissolved gases in water on metal surfaces have been given. In the second paper a cell was described which consisted of electrodes of aluminum and magnesium in a solution of aluminum sulphate, to which some hydrogen peroxide was added. Aluminum metal behaves in a peculiar manner in contact with dissolved air, or oxygen, and becomes electronegative to a similar aluminum electrode in water free from dissolved air. Magnesium does not show this effect: hence a cell with the two metals for electrodes has a comparatively large E.M.F. developed when dissolved air or oxygen is introduced. The effect is considerably increased by adding hydrogen peroxide. Acting on the suggestion of Professor Bancroft, tests were applied to the water in which clean aluminum had stood for a few hours, and a measurable quantity of hydrogen peroxide was detected. This was developed from the action of the dissolved oxygen on the aluminum, probably according to the following reaction, also suggested by Bancroft :

# $_{2}Al + 6H_{2}O + 6O = Al_{2}(OH)_{6} + 3H_{2}O_{2}$

The amount of yield of the peroxide was considerably increased in several ways. Without dissolved air no trace of peroxide was observed. The generation of the hydrogen peroxide explains the abnormally high E.M.F. developed between two metals so close together in the electrochemical series.

# PHONOGRAPHIC RECORD OF THE DOPPLER EFFECT.<sup>1</sup>

#### BY CHAS. T. KNIPP.

IN this paper an attempt was made to obtain a phonographic record of the Doppler effect. The phonograph was placed at the side of the track, and distant about thirty feet. The horn was directed toward the moving source of sound. A record was taken of a continuous blast of the locomotive whistle sounded over a distance of about 1,000 feet — 500 feet on either side of the position of the observer. By simple calculation it can be shown that the pitch will be lowered one tone when the train velocity is 44 miles per hour or 64 feet per second. The train in question was moving at a velocity of 57 miles per hour or 84 feet per second. The pitch accordingly should be lowered 9.3/8 tones. The

#### RADIOACTIVITY OF A SMOKE-LADEN ATMOSPHERE.<sup>1</sup>

#### BY S. J. ALLEN.

THIS paper gives an account of a series of observations on the rate of decay of the radioactivity of the air at Cincinnati, during the last eight months. The atmosphere at Cincinnati is very smoky and it was therefore thought interesting to observe what effect the smoke particles might have on the rate of decay.

An endless copper wire running over two insulated wooden pulleys was suspended about 20 feet from the ground, and could be charged to a high potential by means of a large static machine. The length between the pulleys was about 180 feet, thus giving 360 feet of wire for the activity to be deposited on.

The active substance deposited on this wire was removed and tested for its activity in the usual manner. In some of the observations the rate of leak method was used and in others the activity was measured by means of the new null reading instrument devised by the author and described in an accompanying paper.

The active substance was collected on the wire under three different conditions: (1) The wire was charged negative, (2) the wire was charged positive, (3) the wire was uncharged.

The active substance deposited was removed from the wire in two different ways. Firstly, by rubbing over the wire a piece of leather moistened with ammonia. Secondly, by rubbing over the wire a piece of thin linen without any ammonia. In some other experiments a lead wire about 50 feet in length was suspended from the copper wire, and afterwards removed and wound in a flat spiral and tested without removing its activity.

Under these various conditions we have the total activity which is deposited on a wire; the part which adheres lightly and the part which can be dissolved off with the outside layer of metal.

About fifty decay curves in all were obtained, extending in some cases over many hours.

These curves were then compared with one another and as far as there was any similarity collected into groups. These groups were then examined to see if there was any simple exponential rate of decay common to all or to part of them.

The main facts brought out in this investigation may be briefly summarized as follows:



When uncharged the amount obtained was quite considerable, the maximum in this way being as great as 25 per cent. of the maximum obtained when the wire was charged negatively.

2. The decay curves obtained differed widely, both with regard to one another of the same method of collection, and to ones of different methods; the period of decay (time taken to fall to have value) varying from 30 to 80 minutes.

3. Only two simple exponential curves could be obtained which extended over any appreciable length of time. One gave a period of about 38 minutes and the other a period of 30 minutes. About one third' of the curves were approximately exponential and had a period from 36to 40 minutes. There thus seems to be a period of decay of about 38 minutes. The rest of the curves were very irregular and had no common characteristic for any length of time. Some of them decayed rapidly at first and then more slowly, whilst others behaved just the reverse.

4. At least eight or ten of the curves showed a slow rate of leak remaining for many hours. In two or three cases this rate of decay was identified with that of thorium excited, having a period of decay of about 11 hours. The fact was brought out that the thorium excited was not always present, and in very variable quantities, the amount in some cases rising to 30 or 40 per cent. of the total. It was found on the uncharged as well as on the negatively charged wire, though in larger quantities in the latter case, and especially when the wire was charged for a number of hours.

5. Whenever possible the amount of thorium excited present was estimated, and this subtracted from the actual curve, and a new curve free from thorium excited plotted. The majority of these new curves give a period of from 28 to 38 minutes. Two of them were almost exactly exponential with a period of 28 minutes, two gave a period of 38 minutes and were nearly exponential, while two had at first a period of 52 minutes, then changing to one of about 28 minutes.

1. On one occasion the activity of the uncharged wire was removed and the wire then charged negatively for an hour. The two curves obtained were in general characteristics similar, and both showed the presence of thorium excited.

One may I think conclude from these results that there is a simple exponential decay with a period of 28 minutes, another one of 38 minutes, and some evidence of a much slower rate of decay with a period of over 50 minutes. If the period is over 60 minutes one  $c_{an}$  be certain that thorium excited is present. The period of 28 minutes agrees with that of radium. The results of this paper then show that in general the doubtedly the same as that of snow, and rain, as observed by other experiments, though the rate of decay is in general different.

UNIVERSITY OF CINCINNATI,

November, 1907.

## An Investigation of the Optical Properties of Films of Magnetic Metals.<sup>1</sup>

#### BY C. A. SKINNER AND A. Q. TOOL.

THIS paper deals with the magnetic rotation and ellipticity produced by films of iron, cobalt, and nickel of definite thicknesses together with the refractive indices, reflection and transmission of the same.

It appears that two distinct types of films may be produced by cathode deposit *in vacuo*, one a *metallic* the other a *dark* film. The difference does not arise from the gas in which the films are produced for they are alike, whether hydrogen, nitrogen or helium be used as gas filling.

The optical properties of these different types are quite different, and they also differ from those obtained by electrolytic deposition. Both iron and cobalt in the *metallic* type possess magnetic rotary power four times as large as the electrolytic films, while the *dark* types exhibit a rotary power remarkably smaller than the electrolytic. The ellipticity imparted to the transmitted ray is affected to an equal degree.

Dark films of iron have an absorption region in the blue and in this region the magnetic rotation and ellipticity reverse their directions, as might be predicted from the characteristics exhibited by other substances possessing an absorption region in the visible spectrum. Dark films of cobalt show also interesting results in the visible spectrum, which duplicate in a sense the results from the iron.

Only *metallic* films of nickel could be obtained and these exhibited effects almost too small to measure.

<sup>1</sup>Abstract of a paper presented at the Chicago meeting of the Physical Society, December 30, 1907, to January 2, 1908.



## 1 H E

## PHYSICAL REVIEW.

A COMPARISON OF THE FORMULAS OF HELMHOLTZ AND NERNST FOR THE ELECTROMOTIVE FORCE OF CONCENTRATION CELLS.

BY HENRY S. CARHART.

### **TEMPERATURE** COEFFICIENTS.

A N instructive series of relations, expressing the several quantities as a function of the temperature, will serve as a fitting point of departure for this paper. These relations are the following:  $P = P_0(1 + at)$ , for the pressure of a gas at constant volume.  $p = p_0(1 + at)$ , for osmotic pressure.  $R = R_0(1 + at)$ , for the resistance of pure metals.  $E = E_0(1 + at)$ , for electrolytic thermo-electromotive force of infinitely dilute solutions.

The coefficient a has the same value in all four equations. It is 1/273 or 0.00366 very approximately, at least for the pressure of an ideal gas, most nearly represented by hydrogen; for the resistance of pure platinum; and for the E. M. F. of any concentration cell with solutions indefinitely dilute. It is an interesting inquiry as to what is the common relationship indicated by the common constant a equal to 1/273.

The differential coefficient of pressure with respect to temperature from the first equation is  $dP/dT = P_0 a$ ; from which we have  $a = I/P_0 \cdot dP/dT$  as the most general expression for the temperature coefficient, with corresponding expressions for the other three relations.

If now P, for example, is zero at the absolute zero of tempera-

ture, then  $0 = P_0(1 - 273a)$  and  $a = 1/273 = 1/T_0$ . Substitute this value of a in the equation above, and  $dP/dT = P_0/T_0$ . Whence  $P_0 = T_0 \cdot dP/dT$ . Similarly in general,  $P = T \cdot dP/dT$ ; that is, the pressure is proportional to the temperature on the absolute scale. Corresponding expressions may be derived for the other quantities. If R is zero at the absolute zero of temperature, then  $R = T \cdot dR/dT$  and  $a = 1/T_0$ . So also if E is zero at the zero of the absolute scale, then  $E = T \cdot dE/dT$  and a for that relation is also  $1/T_0$ .

If in each of the four relations the quantity represented becomes zero at the zero of the absolute scale, on the assumption that the law holds down to that point, then the temperature coefficient a is  $I/T_0$ . Each equation may then serve to define and evaluate the absolute zero; and if this zero denotes anything real, such as the zero of heat energy, then the  $T_0$ 's for the several equations may be expected to coincide. As a matter of fact, the coefficient a is practically the same in all four equations, and the corresponding absolute zeros are therefore approximately identical.

In the case of pure platinum Dewar and Fleming have extended experimentally the straight line graph connecting its resistance and temperature so far down the scale toward absolute zero that they are able to say that it runs nearly through  $-273^{\circ}$  C. The common constant *a* means that gas pressure (volume constant), osmotic pressure, electrical resistance, and electromotive force (under definite conditions) are all proportional to the absolute temperature.

If R has a positive value at the absolute zero, as it has in the case of alloys, then

$$R = R_{-273} + T \frac{dR}{dT}.$$

 $R_0$  is then greater than  $T_0 \cdot dR/dT$  and *a* is less than  $1/T_0$ . So also *E* at the absolute zero may have either a positive or a negative value, and then

$$E = E_{-273} + T \frac{dE}{dT}.$$

### THE HELMHOLTZ EQUATION.

The famous Helmholtz equation for the electromotive force of a voltaic cell is



$$E = \frac{H}{nF} + T\frac{dE}{dT}$$

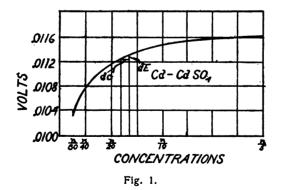
corresponding with the last equation above. In the Helmholtz equation H is the heat of reaction or of dilution, expressed in joules; n is the valence of the cation; and F is the number of coulombs transported by a gram-equivalent of the cation.

The term  $T \cdot dE/dT$ , proportional to the absolute temperature, is purely thermo-electric. It is now fully established and agreed that the coefficient dE/dT is the algebraic sum of the electromotive forces per degree arising at the several thermal junctions in the cell. If this coefficient is positive, then the cell converts some of the heat of the cell and its surroundings into the energy of an electric current; if it is negative, the electrical energy given out is less than the heat of reaction and dilution, and the cell heats. In the former case heat is absorbed and utilized; in the latter it is generated and wasted.

The second term of the Helmholtz equation denotes then thermoelectromotive force, and so does any other form of expression for electromotive force which is proportional to absolute temperature.

THE NERNST EQUATION FROM THERMO-ELECTROMOTIVE FORCE.

The curve in the accompanying figure exhibits the relation between the concentration of the electrolyte (CdSO<sub>4</sub> + H<sub>2</sub>O) and the



electromotive force per degree C. The electrodes were the same cadmium amalgam in every case, the only variation being the con-

centration of the electrolyte.<sup>1</sup> From this curve one may write the equation connecting electromotive force and concentration as follows:

$$dE = bT \frac{dc}{c}.$$

In this equation b is a proportionality factor and c is the concentration. Integrating,

$$E = bTlnc + a$$
 constant.

But when T is zero E is zero, and therefore the integration constant is zero. Therefore E = bTlnc (*In* is the natural logarithm). This expression is the potential difference arising at a single electrode. For a cell with different concentrations of the same electrolyte at the two electrodes, the E.M.F. is the difference between the two electrode potentials, or

$$E = bTlnc_2 - bTlnc_1 = bTln\frac{c_2}{c_1}.$$

It will be recognized that this equation agrees in form with that of Nernst for the E.M.F. of a concentration cell :

$$E = \frac{R}{nF} T ln \frac{c_2}{c_1}.$$

The Nernst equation, or its equivalent above, is only a variation of the second term of the Helmholtz equation; for the differential coefficient of E with respect to T from the first equation above is

$$\frac{dE}{dT} = bln \frac{c_2}{c_1}$$
, and  $b = \frac{dE}{dT} \div ln \frac{c_2}{c_1}$ .

Substitute this value of b in the equation for E, and we have

$$E = T \frac{dE}{dT}.$$

The Nernst equation is therefore only another form of expression for that part of the E.M.F. of a concentration cell arising from electrolytic thermo-electromotive force; and it gives the correct value for the E.M.F. of such a cell only for infinite dilution, or when the

<sup>1</sup> Trans. Amer. Electrochemical Soc., Vol. II., p. 126; also PHYS. REV., Vol. XXV., p. 357.

heat of dilution is negligible. When there is no heat of dilution, the first term of the Helmholtz equation is zero and only the term expressive of thermo-electromotive force remains.

THE RESEARCH OF RICHARDS AND FORBES.

These conclusions find ample justification in two directions :

1. In the research of Richards and Forbes, published by the Carnegie Institution of Washington, and entitled "Energy Changes Involved in the Dilution of Zinc and Cadmium Amalgams."<sup>1</sup>

2. In the preliminary results of a research now in progress in my laboratory under the skilled hand of Mr. F. J. Mellencamp. In this research the observed and computed electromotive forces are compared for concentration cells with solutions of any degree of dilution.

The research of Professor T. W. Richards and Mr. Forbes is a thorough, careful and admirable piece of work. They measured the electromotive force of concentration cells in which the difference of concentration was in the amalgams composing the electrodes, an electrolyte of one concentration only being employed. The heat of dilution of the amalgams was measured directly by a special calorimeter. The dilution of a 0.9 per cent. zinc amalgam with an equal weight of mercury *absorbed* heat at the rate of 52 joules per gram-molecule of zinc ; that is, the dilution of zinc amalgam has a cooling effect. The heat of dilution of a 3 per cent. cadmium amalgam was so small as to defy direct measurement, but it is probably slightly positive ; that is, the dilution of cadmium amalgam generates heat.

The authors say on page 60: "One of the striking facts in relation to cadmium amalgam is the fact that its heat of dilution is so small as to be negligible. Therefore, the equation of Helmholtz reduces practically to the form

$$E=T\frac{dE}{d\tilde{T}},$$

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$$E_0 = T_0 \frac{dE}{dT},$$

the coefficient

$$\frac{1}{E_0}\frac{dE}{dT} = \frac{dE}{dT} \div T_0 \frac{dE}{dT} = \frac{1}{T_0}$$

The agreement of this coefficient with that of gas pressure signifies merely that the electromotive force is very approximately proportional to T, the absolute temperature, for then a always equals 1/273 or 0.00366.

The accuracy of the work of Richards and Forbes is attested by the fact that the measured temperature coefficient for the cadmium amalgams is very close to 0.00366. On this point I quote the following:

"It becomes now a matter of great interest to compare this change of potential with the requirements of the gas law, by comparing the temperature coefficient with the temperature-pressure coefficient of a perfect gas over the same range of temperature.

"The following table gives the temperature coefficients referred to the observed potentials at zero:

2-4, from 30° to 15.2°.

 $\frac{1}{E_0}\frac{\Delta E}{\Delta T} = \frac{0.001659}{14.8 \times 0.030826} = 0.00364$ 

2-4, from 15.2° to 0.0°.

$$\frac{1}{E_0}\frac{\Delta E}{\Delta T} = \frac{0.001719}{15.2 \times 0.030826} = 0.00367$$

1-4, from 30° to 15.2°.

$$\frac{1}{E_0}\frac{\Delta E}{\Delta T} = \frac{0.002578 \times 288.2}{14.8 \times 0.050332 \times 273} = 0.003665$$

1-3, from 30° to 15.2°.

$$\frac{1}{E_0} \frac{\Delta E}{\Delta T} = \frac{0.00177 \times 288.2}{14.8 \times 0.03413 \times 273} = \frac{0.00366}{0.003656}$$
Average



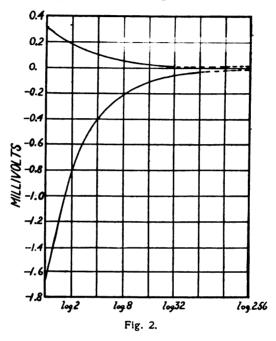
of temperature is identical with the increase of pressure of a perfect gas."

These remarks and others of similar import lead one to the conclusion that Professor Richards regards this agreement of the electromotive force coefficient with the pressure coefficient, both with respect to temperature, as a proof that the gas law, pv = RT, applies to a concentration cell. On the contrary it appears from this discussion that this agreement of coefficients means only that the electromotive force of a concentration cell, with negligible heat of dilution, is proportional to the absolute temperature.

It is particularly unfortunate that these investigators did not determine the temperature coefficient for pairs of zinc amalgams, for it is certain that they would have found a value greater than 0.00366 except in the case of very dilute amalgams. They did *calculate* one temperature coefficient for zinc amalgams and found it to be 0.00379.

The identity of the temperature coefficient with 1/273 is not a satisfactory proof even that the heat of dilution is negligible, for the electromotive force due to heat of dilution affects only the value of  $E_0$  in the expression for the temperature coefficient,  $1/E_0 \cdot dE/dT$ , and a moderately small change in the denominator of a small fraction produces a nearly negligible change in the value of the fraction itself.

A better criterion to apply as a test of the presence or absence of heat of dilution is to compare the measured values of electromotive force with those derived from the expression  $T \cdot dE/dT$ , or its equivalent in the form of the Nernst equation. This method is beautifully illustrated in Fig. 2, copied from the paper of Richards and Forbes. The logarithms of the concentration ratios are plotted as abscissas and the deviations of the observed electromotive forces from the theoretical values given by the Nernst equation as ordinates. It will be observed that the electromotive forces for the zinc amalgams are smaller than the values derived from the Nernst formula, while those of the cadmium amalgams are larger. MoreBoth of these deviations are completely and satisfactorily explained by the appreciable negative heat of dilution of zinc amalgams and the very small positive heat of dilution of the amalgams of cadmium. When the heat of dilution is negative, the first term of the Helmholtz equation is also negative, and the E.M.F. of the



cell is less than  $T \cdot dE/dT$ . When the heat of dilution is positive, the first term of the Helmholtz equation is positive, and the E.M.F. of the cell is greater than  $T \cdot dE/dT$ . Since the Nernst equation is only the equivalent of the second term of the Helmholtz equation, the deviations of the curves in Fig. 2 from the straight line, which they both approach asymptotically, are completely explained by the first term of the Helmholtz equation, derived from the heat of dilution.

It is therefore useless to attempt to correct the Nernst formula so as to make it cover the case of concentration cells in which there is heat of dilution to affect the value of the E.M.F. It applies only to cells with infinite dilutions. The second term only of the Helmholtz equation is proportional to the absolute temperature. The first term,

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while not necessarily independent of temperature, is not proportional to it and cannot therefore be included in the Nernst equation or in any modification of it, unless another term is added. Richards and Forbes appear to miss entirely the cause of the deviations of the observed electromotive forces from the values computed by the Nernst equation, and their speculations relative to the cause of these deviations are thus of little practical value. The reason for them lies directly on the surface, and it has probably been missed because of the point of view from which the research was carried out.

## THE RESEARCH OF CARHART AND MELLENCAMP.

The preceding conclusions, involving a comparison of the Helmholtz and Nernst equations, are completely justified by the measurements on a series of concentration cells made with solutions of electrolytes whose heats of dilution are known. In most of these cases the concentrations are such that the heats of dilution are relatively large, and the first term of the Helmholtz equation can not be neglected. No better justification of the Helmholtz equation than these results has ever been presented.

Whenever the heats of dilution of the solutions in the two legs of a concentration cell differ, the difference is available as energy to produce electromotive force, represented by the first term of the Helmholtz equation. The electrode in the more dilute solution is the anode. Let us suppose the quantities of the two solutions so large that the entrance of a gram-equivalent of the metal at the anode and the removal of an equal quantity from the solution about the cathode do not change the concentrations of the solutions. Then when a gram equivalent of the metal at the anode becomes a salt, it is diluted down to the same concentration as that of the solution surrounding the anode; at the same time a gram-equivalent of the same metal is removed from the more concentrated solution surrounding the cathode. This latter operation absorbs less energy than is derived from the former, if the heat of dilution is positive; and this surplus energy is available to produce electromotive force.

To illustrate: One gram-molecule of  $ZnSO_4.20H_2O$  diluted to  $ZnSO_4.50H_2O$  generates 318 calories of heat (Thomsen). Also,  $ZnSO_4.20H_2O$  diluted to  $ZnSO_4.400H_2O$  generates 400 calories.

Hence,  $ZnSO_4.50H_3O - ZnSO_4.400H_3O$  is equivalent to the difference between 400 and 318, or 82 calories. If a cell is set up with these two solutions, the E.M.F. corresponding to this difference in the heats of dilution is

$$\frac{82 \times 4.186}{2 \times 96,550} = 0.00178$$
 volt.

The coefficient dE/dT of a cell set up with electrodes of liquid zinc amalgam in the above solutions is positive and equal to 0.0000528, as a mean of several determinations. Hence, for 25° C. the term  $T \cdot dE/dT$  is 298 × 0.0000528 = 0.01573. Then

$$E = 0.00178 + 0.01573 = 0.0175$$
 volt.

The observed E.M.F. at 25° was 0.0171.

In the following table  $E_{\lambda}$  is the E.M.F. due to the heat of dilution, and  $T \cdot dE/dT$  is the E.M.F. derived from the heat of the surroundings, except in the last example where it is negative.

Solutions.	dE dT	$T \frac{dE}{dT}$	EA	Comp. E.M.F.	Obs. E.M.F.
ZnSO <sub>4</sub> . 50 H <sub>2</sub> O ZnSO <sub>4</sub> . 400 H <sub>2</sub> O	0.0000528	0.01573-25°	0.00178	0.0175	0.0171
$ZnSO_4$ . 100 H <sub>2</sub> O $ZnSO_4$ . 400 H <sub>2</sub> O	0.000032	0.00954-25°	0.00072	0.0103	0.0101
ZnSO <sub>4</sub> . 50 H <sub>2</sub> O ZnSO <sub>4</sub> . 100 H <sub>2</sub> O	0.0000174	0.00518-25°	0.00106	0.0062	0.0062
ZnSO <sub>4</sub> . 50 H <sub>2</sub> O ZnSO <sub>4</sub> . 200 H <sub>2</sub> O	0.0000344	0.01025-25°	0.00145	0.0117	0.0116
CdSO4 . 50 H2O CdSO4 . 400 H2O	0.0000188	0.00557–23°	0.01080	0.0164	0.0164
CdSO4 . 50 H2O CdSO4 . 200 H2O	0.000009	0.00246–0°	0.00847	0.0109	0.0108
CdSO4 . 100 H.O CdSO4 . 400 H2O	0.0000155	0.00423–0°	0.00604	0.0103	0.0099
$CuSO_4 . 60 H_2O$ $CuSO_4 . 200 H_2O$	0.0000248	0.00739-25°	0.00251	0.0099	0.0098
ZnCl, . 21.9 H,O			!		!

The last case furnishes a specially instructive illustration of the principles involved, because the temperature coefficient is negative, as in most voltaic cells. The E.M.F. of this cell is accordingly less than the value derived from the heat of dilution. The concentrations of the solutions of zinc chloride were determined by titration, and the corresponding heats of dilution by interpolation by means of a smooth curve plotted from recorded measurements.

In the case of the sulphates, the E.M.F. due to heat of dilution runs from 7 to 78 per cent. of the whole E.M.F. of the cell.

The temperature coefficients of the above concentration cells, referred to the observed electromotive force at zero, are the following in the order of the table : 0.00335, 0.00344, 0.00301, 0.00320, 0.00118, 0.00083, 0.00156, 0.00270, 0.00138. These coefficients do not look very much like a confirmation of the requirements of the gas law. The temperature coefficient is not 0.00366 simply because the E.M.F. of these cells is not in any case proportional to the absolute temperature.

UNIVERSITY OF MICHIGAN, December, 1907.

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## A VARIATION OF THE BJERKNES ANALOGY BETWEEN HYDRODYNAMIC AND ELECTRIC OR MAGNETIC FIELDS.

#### BY A. P. WILLS.

I. INTRODUCTORY.

### 1. The Bjerknes Analogy.

IN the hydrodynamic analogy to electric or magnetic fields developed by Professor V. Bjerknes,<sup>1</sup> following out and extending the ideas of his late father, Professor C. A. Bjerknes, he makes the velocity of the fluid correspond to the electric or magnetic flux, the specific momentum (momentum per unit volume) to the electric or magnetic field intensity, and the specific volume to the electric or magnetic inductivity.

Employing this correspondence, he shows that there is a complete geometric analogy between the vectors representing the velocity and specific momentum in the hydrodynamic field and the vectors representing the flux and the field intensity in the electric or magnetic field, the analogy extending to stationary phenomena. Expressed in other words, he finds for stationary (including static) phenomena that the relationship of the vectors representing the velocity and specific momentum is expressed by a system of equations formally identical with that representing the relationship of the vectors corresponding to the flux and field intensity in the electric or magnetic field. The dynamic analogy found is not quite so complete; for although the expression for the resultant mechanical force acting upon a body in the hydrodynamic field can be given a form in which the individual terms are of the same type as the corterms are opposite. Various forms of expression are found for the elementary mechanical force acting per unit volume at any point of the fluid, and among these there is one which has, except for the reversed sign, precisely the analogous form to that given by Heaviside for the corresponding case in the electric or magnetic field.

The analogy which will be developed here, and which, for reasons which become obvious later, will be termed the change-of-state analogy, has many properties in common with the Bjerknes analogy, and on this account a brief summary of some of the cardinal features of the latter will now be given.

Corresponding to the ether, there is in the Bjerknes analogy the fundamental fluid, and corresponding to the material bodies of different inductivities there are the fluid bodies. The fluid bodies are in general of different density than the fundamental fluid, in which they are supposed to be immersed, and in general the properties of motion of the fluid constituting a *fluid body* are quite different from those associated with the *fundamental fluid*. Difference in density of course implies difference in specific volume, and this latter guantity corresponds to electric or magnetic inductivity. In accordance with this then, a *fluid body* of greater density than the *fundamental* fluid would in the magnetic case correspond to a diamagnetic body, while a *fluid body* of less density than the *fundamental fluid* would correspond to a paramagnetic body. (Just the reverse is the case in the change-of-state analogy.) An important difference between the Bjerknes analogy and the change-of-state analogy lies in the fact that in the Bjerknes analogy a *fluid body* is always constituted of the same particles of fluid, and this is also true for the fundamental fluid; but in the change-of-state analogy a particle of fluid may at one instant be a constituent of the fundamental fluid and later a constituent of some fluid body.

Referring still to the Bjerknes analogy, we have next to notice the conditions which have to be fulfilled at a surface of separation. If the analogy in this respect is to hold, the normal components of the velocity and the tangential components of the specific momentum must pass through the surface continuously (it being supposed that in the electric or magnetic case there is no true surface charge). The former of these conditions requires in general that the surface of a fluid body shall be constantly changing its configuration and position in space, so that a *fluid body* would not strictly correspond to a material body in the electric or magnetic field, since the latter remains at rest. This difficulty is surmounted by supposing the fluid motion to be of a vibratory nature, consisting of small vibrations about a mean configuration, so that the fluid bodies may appear to be at rest. The hydrodynamic vectors which correspond to the electric and magnetic vectors, and which describe the vibratory motion, are mean values of the actual periodically varying vectors. These mean vectors satisfy the boundary conditions; but owing to a peculiar property of the fluid motion, the analogy only extends to static electric or magnetic fields. In the change-of-state analogy the boundary conditions do not introduce the difficulty just considered.

We have noticed here only some of the chief features of the Bjerknes analogy, but in developing the change-of-state analogy we shall frequently recur to it.

## 2. The Change-of-State Analogy.

As mentioned above, the change-of-state analogy has much in common with the Bjerknes analogy. The mathematical developments pertaining to each are very similar. In thinking and working on the new form of analogy I have been much benefited by many conversations with Professor Bjerknes, also by his letters and writings, and I have pleasure in acknowledging my indebtedness to him in this connection. I have made free use of the methods of Professor Bjerknes, and I have also employed, in large measure, his notation, which is most admirably adapted to the purposes in view.

In the change-of-state analogy the scheme of correspondence between the hydrodynamic quantities, on the one hand, and the electric or magnetic quantities, on the other, is the following :



It will be remembered that in the Bjerknes analogy velocity corresponds to flux, specific momentum to field intensity, and the reciprocal of density (specific volume) to inductivity. By the term specific momentum is to be understood the momentum per unit volume.

We have now to imagine the fluid system which is to correspond in the change-of-state analogy to a stationary electric or magnetic svstem. The fluid system which we consider consists of a fundamental fluid corresponding to the ether, and of fluid bodies corresponding to material bodies in the electric or magnetic field. In cases where it is not necessary to discriminate between the fundamental fluid and the fluid of a fluid body we shall simply use the term The fundamental fluid is supposed to be of infinite - the fluid. extent, being bounded by the stationary closed surfaces of the regions containing the *fluid bodies* and the surface of the infinite sphere. A fluid body consists of fluid within one of these closed surfaces, and differs from the *fundamental fluid* in that it is compressible, and that the characteristics of motion of the fluid in it are quite different and not so simple as in the fundamental fluid; furthermore the density of the fluid in a *fluid body* may be variable from point to point and in general different from that of the fundamental fluid. Fluid may cross the surface of the region bounding a *fluid body* (the surface of the *fluid body*). Upon doing so it is supposed to suddenly change its state. Thus if it is fluid which enters the region of a fluid body it suddenly loses the state of motion characteristic of the fundamental fluid, and acquires that which is characteristic of the fluid body; and associated with this change of state there is in general a change of density. In a similar way, fluid which escapes from the region of a *fluid body* loses the properties of the *fluid body*, and acquires those of the fundamental fluid. (It is not necessary, for the purposes in view, to specify the nature of the mechanism which would produce the changes at the surface of the *fluid body* which are supposed to occur.) From the preceding remarks it appears that a given particle of fluid may at one time be a constituent part of the fundamental fluid, and at another time a part of a fluid body. If in its wanderings it chances to cross the surface of a fluid body, it will suddenly change its state - lose certain properties and A. P. WILLS.

acquire new ones. When a portion of fluid constitutes a part of the *fundamental fluid*, it is said to be in the *fundamental state*, and when it constitutes part of a fluid body it is said to be in the *body state*.

Boundary Conditions. — The two boundary conditions which have to be fulfilled in the change-of-state analogy are :

I. At any surface of separation the normal components of the specific momentum must be continuous, if it be supposed that no accumulation of mass occurs at the surface.

2. At any surface of separation the tangential components of the velocity must be continuous.

The principle of the conservation of mass requires that the first of these conditions be fulfilled. For, if there is to be no accumulation of mass at the surface of separation, the mass of fluid which arrives per unit area per unit time at one side of the surface must be equal to the corresponding mass which leaves the surface on the other side; and the expression of this fact requires the continuity of the normal components of the specific momentum.

With regard to the second boundary condition, it has simply to be remarked that the sudden change in density which is supposed to occur at the surface of separation does not implicitly require the assumption of an infinite tangential force, and hence we suppose none such to be present there; it follows then that there can be no finite change in the velocity tangential to the surface of separation as the fluid crosses the surface, or, in other words, that the tangential components of the velocity are the same on both sides of the surface.

A concrete illustration of the sort of change which is supposed to occur at the surface of a fluid body is furnished by the familiar phenomenon of condensation, or of evaporation.

Induced and Energetic Vectors. — In the theory of electricity and magnetism it is customary to consider the actual field intensity and the actual flux at any point as made up of two parts: (1) A part

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ing to the second part are called energetic vectors. Intrinsic polarization of a permanent magnet, sources of thermoelectric force, or of contact electric force, are examples of energetic sources. The energy of an electric or magnetic field is established primarily through energetic sources; and hence Professor Bjerknes has adopted the term — energetic vectors — for vectors relating to intrinsic sources. In a similar way, the actual hydrodynamic vectors may be considered as made up of induced and energetic parts.

Hydrodynamic Notation. — The notation employed in the changeof-state analogy to designate the actual, induced, and energetic vectors, and the density of the fluid is given in Table I.

BLE	

Quantity.	Actual.	Induced.	Energetic.
Sp. momentum	С	C,	C,
Velocity	Ca	C	C,

Density of fluid  $-\gamma$ .

Among the six vectors given in Table I. there are four independent relations which constitute what are called the equations of connection and which will be given presently.

Elementary vector methods are employed in the mathematical work which follows, on account of the great saving of space which is thereby secured. The notation is essentially that used in Gibb's Vector Analysis.

## II. DEVELOPMENT OF THE EQUATIONS FOR THE HYDRODYNAMIC SYSTEM IN THE CHANGE-OF-STATE ANALOGY.

In order to obtain a comprehensive idea of the nature and properties of the hydrodynamic system which is employed in the changeof-state analogy, we shall first investigate the properties of the hydrodynamic field. Afterwards the properties of this hydrodynamic field will be compared with those of the stationary electric or magnetic field.

*Equations of Connection.* — Among the vector quantities found in Table I. there is the following set of equations of connection :

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$$C = C_i + C_e,$$
  
 $c_a = c + c_e,$   
 $C_i = \gamma c,$   
 $C_e = \gamma c_e.$ 

Remembering that the actual specific momentum and the actual velocity are each made up of corresponding induced and energetic parts; and that the product of density into velocity gives the corresponding specific momentum, these equations are obviously true.

The Equation of Motion and the Equation of Continuity. — In the development of the properties of the hydrodynamic system which is employed in the change-of-state analogy, the equation for a perfect fluid and the equation of continuity furnish the starting point.

The equation of motion is

(1) 
$$\gamma \frac{d\mathbf{c}_a}{dt} = \mathbf{f} - \nabla p,$$

wherein f denotes the external force acting per unit volume of the fluid, p the pressure, and  $-\nabla p$  the pressure gradient,  $\gamma$  the density, and  $dc_a/dt$  the actual acceleration of a particle of the fluid. The equation states that the kinetic reaction per unit volume of the fluid is equal to the sum of the forces per unit volume due to external agencies and to fluid pressure.

The equation (1) is not at all suggestive of the equations of the electric or magnetic field. But the equation is capable of development into a form which is appropriate to the purposes in view. This development will be given presently.

In writing the equation of motion in the form given, it is tacitly assumed, of course, that the fluid constituting the *fundamental fluid* or any *fluid body* has the properties of a perfect fluid.

To express the condition of conservation of mass we have the equation of continuity,

(2) 
$$-\frac{\partial \gamma}{\partial t} = \operatorname{div} \mathbf{C},$$

In connection with equations (1) and (2), we have occasionally to make use of the Eulerian Operator, which relates the *individual* rate of change of a quantity with the *local* rate of change of the same quantity. This operator is expressed as follows :

(3) 
$$\frac{d(\cdot)}{dt} = \frac{\partial(\cdot)}{\partial t} + \mathbf{c}_{\mathbf{a}} \nabla(\cdot).$$

Proceeding now to the development of equation (1), we express, with the aid of equation (3), the left hand member as follows:

$$\gamma \frac{d\mathbf{c}_a}{dt} = \gamma \frac{\partial \mathbf{c}_a}{\partial t} + \gamma \mathbf{c}_a \nabla \mathbf{c}_a,$$

and referring to the first term on the right of this last expression, we may write

$$\gamma \frac{\partial \mathbf{c}_a}{\partial t} = \frac{\partial (\gamma \mathbf{c}_a)}{\partial t} - \mathbf{c}_a \frac{\partial \gamma}{\partial t},$$

or

$$\gamma \frac{\partial \mathbf{c}_a}{\partial t} = \frac{\partial \mathbf{C}_i}{\partial t} + \frac{\partial \mathbf{C}_i}{\partial t} + \mathbf{c}_a \operatorname{div} \mathbf{C},$$

with the aid of the equations of connection  $(C_1)$  and the equation of continuity (2); hence,

$$\gamma \frac{d\mathbf{c}_a}{dt} = \frac{\partial \mathbf{C}_i}{\partial t} + \frac{\partial \mathbf{C}_a}{\partial t} + \mathbf{c}_a \operatorname{div} \mathbf{C} + \gamma \mathbf{c}_a \nabla \mathbf{c}_a$$

The last term on the right of this expression may be transformed as follows :

$$\gamma \mathbf{c}_a \nabla \mathbf{c}_a = \gamma \mathbf{c}_a \mathbf{C}_a \nabla + (\operatorname{curl} \mathbf{c}_a) \times \mathbf{C}$$
  
=  $\frac{1}{2} \gamma \nabla \mathbf{c}_a^2 + (\operatorname{curl} \mathbf{c}_a) \times \mathbf{C}$   
=  $\nabla \frac{1}{2} \gamma \mathbf{c}_a^2 - \frac{1}{2} \mathbf{c}_a^2 \nabla \gamma + (\operatorname{curl} \mathbf{c}_a) \times \mathbf{C}$ ;

and introducing this value for  $\gamma c_a \nabla c_a$  in the last expression for  $\gamma dc_a/dt$ , we get

$$\gamma \frac{d\mathbf{c}_a}{dt} = \frac{\partial \mathbf{C}_i}{\partial t} + \frac{\partial \mathbf{C}_a}{\partial t} + \mathbf{c}_a \operatorname{div} \mathbf{C} + \nabla \frac{1}{2} \gamma \mathbf{c}_a^2 - \frac{1}{2} \mathbf{c}_a^2 \nabla \gamma + (\operatorname{curl} \mathbf{c}_a) \times \mathbf{C}.$$

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In the preceding discussion we have not specified the induced and energetic vectors beyond the requirements of equation  $(C_1)$ . In the following paragraph further specification of these quantities will be given in such a way that the geometric and dynamic properties of the fluid motion may be shown in a form which will prove suitable for the analogy with the electric or magnetic field.

Further Specification of the Induced and Energetic Vectors. — It is quite allowable to impose any conditions we like upon the induced and energetic vectors which are not in conflict with equations  $(C_1)$ . Let, then, the induced specific momentum satisfy the equation

(5) 
$$\frac{\partial \mathbf{C}_i}{\partial t} = -\nabla(p + \frac{1}{2}r\mathbf{c}_a^2).$$

From equations (4) and (5) it is obvious that the energetic specific momentum must satisfy the equation

(6) 
$$\frac{\partial \mathbf{C}_{a}}{\partial t} = \mathbf{f} - \mathbf{c}_{a} \operatorname{div} \mathbf{C} + \frac{1}{2} \mathbf{c}_{a}^{2} \nabla \gamma - (\operatorname{curl} \mathbf{c}_{a}) \times \mathbf{C}.$$

### 3. Geometric Properties of the Hydrodynamic Field.

By taking the curl of both members of equation (5) and then reversing the order of the operations of differentiation and curl on the left, it is seen that

(7) 
$$\frac{\partial}{\partial t} (\operatorname{curl} \mathbf{C}_i) = 0.$$

Integration of equation (7) gives

(8) 
$$\operatorname{curl} \mathbf{C}_i = -\mathbf{K},$$

where **K** is a quantity which is independent of the time, and called by Professor V. Bjerknes the *density of the dynamic vortex*. The condition imposed upon the induced motion through equation (5) is such as to require the dynamic vortex density at any point to be invariable; and hence, if the dynamic vortex density is initially zero at all points of a given region, no dynamic vortex motion will ever exist in this region.

It is an interesting fact that the property of conservation of the dynamic vortex motion is likewise present in the hydrodynamic system employed in the Bjerknes form of the analogy.



For purposes of the analogy which we have in view it is important to introduce a quantity called by Professor Bjerknes the *kinematic vortex density*. This is simply the negative of the curl of the induced velocity and is designated by  $\mathbf{k}$ ; thus

$$(C_{\mathbf{z}}) \qquad \qquad \operatorname{curl} \mathbf{c} = -\mathbf{k}.$$

The kinematic vortex, unlike the dynamic, is not subject to conservation in general; but if the motion throughout the system is steady, then the kinematic vortex motion will be conserved. It is an important quantity in that it corresponds to current in the electric or magnetic field.

Another important quantity with which we shall have to deal is the divergence of the specific momentum, designated by H; thus

$$(C_s) \qquad \qquad \text{div } \mathbf{C} = H_s$$

It is important in that it is the quantity which corresponds to the density of electricity or of magnetism in the electric or magnetic field. From the equation of continuity (2) it is evident that it represents the local time rate of decrease of the density of the fluid at any point.

An important property of the energetic motion is easily established for a region throughout which certain conditions are fulfilled. These conditions are the following: (1) The external forces shall vanish, (2) the fluid shall be homogeneous, (3) the fluid shall be incompressible, (4) the dynamic vortex density shall vanish, (5) the energetic velocity shall be initially zero.

Condition (4) is equivalent to requiring that initially no dynamic vortex motion be present in the region, on account of the property of conservation of the dynamic vortex density which we have noted above. Furthermore, since the density of the fluid is constant, according to conditions (2) and (3), and since the dynamic vortex density in this case will be proportional to the kinematic, the density of the fluid being the factor of proportionality, it follows that condition (4) is equivalent to requiring the kinematic vortex density to vanish throughout the region. On account of the first four conditions, it is easily seen that equation (6) for the region in question reduces to

$$\frac{\partial \mathbf{C}_{e}}{\partial t} = -(\operatorname{curl} \mathbf{c}_{e}) \times \mathbf{C};$$

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from which it appears that if the energetic velocity be initially equal to zero throughout the region, then the energetic specific momentum must be always equal to zero throughout the region. In making this deduction it has to be observed that the energetic specific momentum is simply proportional to the energetic velocity, the density of the fluid being a constant factor of proportionality.

As a result of the investigation with which we have just been occupied, it is evident that no inconsistency will be involved in requiring the fluid in a given region to satisfy the following conditions: (1) The fluid shall be homogeneous, (2) the fluid shall be incompressible, (3) the kinematic vortex motion shall vanish, (4) the energetic specific momentum shall vanish.

The properties of the induced and the energetic motions which we have touched upon here will be of service in defining the properties of the *fundamental fluid* and the *fluid bodies*.

### 4. The Fundamental Fluid and the Fluid Bodies.

In accordance with the introductory remarks at the beginning of this paper, it will be remembered that the fluid system which is considered is constituted as follows: There are supposed to exist certain fixed regions bounded by closed surfaces, within which the fluid motion is in general different from that in the fluid which surrounds these regions and which is supposed to have the same properties throughout and to extend to infinity. These regions are referred to as the *fluid bodies*, and the surrounding fluid is called the fundamental fluid. It should be recalled that the fundamental fluid in crossing the surface of a body inwards experiences in general a sudden change in density, in fact loses the characteristic properties of the fundamental fluid; and in a similar way fluid which escapes from a region defining a *fluid body* suddenly acquires the properties of the fundamental fluid. According to this conception, the region containing the fundamental fluid and the regions defining the fluid bodies are filled with the same fluid, the difference in the regions arising from the differences in the character of the motion and the physical state of the fluid when it is in what we may call the fundamental region and when it is within a region defining a body. A fluid body, then, is a region in which the density of the fluid is in

general different from that of the fluid in the fundamental region, and whose state of motion is also different. Whether a given part of the fluid constitutes a part of the *fundamental fluid* or of a *body*, depends on its *state* at the time considered.

The conditions characterizing the state of the *fundamental fluid* may be expressed by the following group of equations, in accordance with the results of the preceding section :

(C<sub>4</sub>) (1) 
$$\gamma = \gamma_0 = \text{const.}$$
, (2)  $H = 0$ ,  
(3)  $\mathbf{k} = 0$ , (4)  $\mathbf{C}_* = 0$ .

These equations respectively require that the *fundamental fluid* be homogeneous; that it be incompressible; that it support no kinematic vortex motion; and that throughout it the energetic specific momentum shall always vanish. These conditions being fulfilled for the *fundamental fluid*, it will never experience any external force (see eq. (6)).

It will presently appear that a set of equations exactly corresponding to equations  $(C_4)$  is used in characterizing the ether for the case of the stationary electric or magnetic field.

A *fluid body* differs from the *fundamental fluid* in that none of the restrictive conditions expressed by equations  $(C_4)$  is impressed upon it.

## 5. The Dynamical Properties of the Fluid Motion.

In considering the dynamical properties of the fluid system employed in the change-of-state analogy it turns out that the character of the fluid motion is more general than is required. The condition is therefore introduced that the energetic specific momentum shall at all points of the system be locally conserved. This requirement is expressed by writing

(9) 
$$\frac{\partial \mathbf{C}}{\partial t} = 0$$

In order that this condition may be fulfilled, it is necessary, on account of equation (6), that

$$\mathbf{f} = \mathbf{c}_a \operatorname{div} \mathbf{C} - \frac{1}{2} \mathbf{c}_a^2 \nabla \gamma + (\operatorname{curl} \mathbf{c}_a) \times \mathbf{C}.$$

This equation gives the force per unit volume exerted by agencies exterior to the fluid system upon the fluid system; and  $-f (= f_{h})$ ,

say) will be the corresponding force exerted by the fluid against the exterior agencies. We thus have

$$(C_{\mathfrak{s}}) \qquad \mathbf{f}_{\mathfrak{s}}' = -\mathbf{c}_{\mathfrak{a}} \operatorname{div} \mathbf{C} + \frac{1}{2} \mathbf{c}_{\mathfrak{a}}^{2} \nabla \gamma - (\operatorname{curl} \mathbf{c}_{\mathfrak{a}}) \times \mathbf{C},$$

expressing the force per unit volume of fluid against exterior agencies.

An expression for the *resultant force* acting upon any *fluid body* is obtained through volume integration of equation  $(C_5)$ . If  $d\tau$  denote an element of volume and  $\mathbf{F}'_{\mathbf{A}}$  the resultant force, then

$$(C_6) \quad \mathbf{F}'_{\mathbf{A}} = -\int \mathbf{c}_a \operatorname{div} \mathbf{C} d\tau + \int \frac{1}{2} \mathbf{c}_a^2 \nabla \gamma d\tau - \int (\operatorname{curl} \mathbf{c}_a) \times \mathbf{C} d\tau,$$

the integrations being extended throughout the whole body.

6. Specifications which Uniquely Determine the Hydrodynamic Field.

In order to preclude the possibility of ambiguity in the comparison of the hydrodynamic field with the stationary electric or the stationary magnetic field, it seems advisable at this point to establish the following theorem :

The hydrodynamic field is uniquely determined when the distributions of the divergence of the actual specific momentum, of the curl of the induced velocity, and of the energetic specific momentum are given.

To establish this theorem we consider first the kinetic energy of the fluid. The kinetic energy of the whole fluid system is represented by either of the equivalent equations

the integrations being extended throughout the whole fluid, which is supposed to extend to infinity, where all the hydrodynamic vectors vanish. In order to avoid the introduction of surface integrals referring to the surface of the fluid bodies, the surface of every fluid body is supposed to be a very thin layer through which the hydrodynamic quantities may vary with extreme rapidity, but yet continuously. At the outside of this surface layer the properties of a fluid body merge into those of the fundamental fluid. With this understanding the energy integral, (10), may be transformed as follows:



No. 3.]

We may write

$$\frac{1}{2}\gamma c_a^2 = \frac{1}{2}\gamma c_a \cdot c_a = \frac{1}{2}C \cdot c_a$$

and we may express the vector **C** as the sum of a lamellar and a solenoidal part, thus

$$\mathbf{C} = -\gamma \nabla \varphi + \operatorname{curl} \mathbf{G},$$

wherein  $\varphi$  is a scalar, and **G** a vector potential; and we may now write

$$\frac{1}{2}\gamma c_a^2 = -\frac{1}{2}C \cdot \nabla \varphi + \frac{1}{2}c_a \cdot \text{curl } G.$$

Substituting this value in equation (10) we get

$$\Psi = -\int \frac{1}{2}\mathbf{C} \cdot \nabla \varphi d\tau + \int \frac{1}{2}\mathbf{C}_a \cdot \operatorname{curl} \mathbf{G} d\tau,$$

which after performing simple vector transformations becomes

It will now be shown that if throughout the fluid system

div 
$$\mathbf{C} = \mathbf{0}$$
,  
curl  $\mathbf{c} = \mathbf{0}$ ,  
 $\mathbf{C}_{\mathbf{c}} = \mathbf{0}$ ,

then the hydrodynamic field must vanish throughout the system. To do this we first notice that if  $C_e = 0$ , then  $c_e$  must also vanish, and that

$$\operatorname{curl} \mathbf{c} = \operatorname{curl} \mathbf{c}_a - \operatorname{curl} \mathbf{c}_s;$$

and since  $c_{e} = 0$  and curl c = 0, that curl  $c_{a}$  must vanish. Now if curl  $c_{a}$  and div C both vanish throughout the system, the total energy,  $\emptyset$ , must also vanish, as is evident from equation (12). The expression for  $\emptyset$  given in equation (11) must also vanish, and since the integral in this expression involves only positive terms, it follows that C must vanish everywhere. Now since C and C, must both vanish everywhere under the given conditions,  $C_{i}(=C-C_{e})$ must also vanish everywhere. Finally, since C,  $C_{i}$  and  $C_{e}$  are necessarily zero at all points of the system, it is evident that the field must vanish completely.

It is now easy to show that any two fields which have the same distribution for the divergence of the specific momentum, the energetic specific momentum, and the curl of the induced velocity, cannot differ in other respects, and that therefore when these quantities are given throughout the fluid the field is uniquely determined.

To do this it is only necessary to consider a third field, the descriptive vectors of which are the differences of corresponding vectors of the two fields considered. It is evident that this third field will be one which has no divergence of the specific momentum, no energetic specific momentum, and no curl of the induced velocity. Now we have just previously seen that such a field must vanish. Hence the two fields considered cannot differ; and it follows that the hydrodynamic field is uniquely determined by the distribution of the divergence of the specific momentum (= the local time rate of decrease of the density), of the energetic specific momentum, and of the curl of the induced velocity (= - the kinematic vortex density).

# III. THE STATIONARY ELECTRIC AND THE STATIONARY MAGNETIC FIELD.

In order to facilitate the comparison of the properties of the hydrodynamic with those of the stationary electric or the stationary magnetic field, a short summary of the properties of the stationary electric and of the stationary magnetic field will be given.

*Electric and Magnetic Notation.*—The notation employed to designate the actual, induced, and energetic vectors, and the electric and magnetic inductivities is given in Table II.

Quantity.		Induced.		Energetic.		
Quantity.	Electric.	Magnetic.	Electric.	Magnetic.	Electric.	Magnetic.
Flux Field inten-	A	B	<b>A</b> i	Bi	<b>A</b> ,	B,
sity	8.	ba	a	ъ	a,	be

TABLE II.

Electric inductivity -a. Magnetic inductivity  $-\beta$ .

Among the six electric vectors given in Table II. there are four independent relations, the equations of connection, which will be given presently; likewise for the magnetic vectors.



### 7. Geometric Properties of the Electric and Magnetic Field.

We will first give a summary of the geometrical properties of the stationary electric and the stationary magnetic field by writing down the appropriate equations which, according to Maxwell's theory, express our knowledge on this subject.

In the first place, there are two groups of equations, one for the electric and one for the magnetic case, which give the relationships among the various flux and field intensity vectors. These equations are referred to as the equations of connection, and are

	$\mathbf{A} = \mathbf{A}_i + \mathbf{A}_e,$		$\mathbf{B} = \mathbf{B}_i + \mathbf{B}_i,$
( <i>A</i> <sub>1</sub> )	$\mathbf{a}_a = \mathbf{a} + \mathbf{a}_a$	( <i>B</i> <sub>1</sub> )	$\mathbf{b}_a = \mathbf{b} + \mathbf{b}_{e},$
	$\mathbf{A}_i = \alpha \mathbf{a}_i$		$\mathbf{B}_i = \beta \mathbf{b}$ ,
	$\mathbf{A}_{\mathbf{a}} = \alpha \mathbf{a}_{\mathbf{a}}$		$\mathbf{B}_{\epsilon}=\beta\mathbf{b}_{\epsilon}.$

The equations which give the magnetic and electric current densities at any point in a stationary electric or stationary magnetic field are

$$(A_2) \qquad \operatorname{curl} \mathbf{a} = -\mathbf{i}, \qquad (B_2) \qquad \operatorname{curl} \mathbf{b} = \mathbf{j}.$$

The first of these equations states that the magnetic current density at any point in a stationary electric field is equal to the curl of the electric induced field intensity at the same point;  $\mathbf{i}$  is a fictitious quantity, since the magnetic conduction current is unknown. The second equation states that the electric current density at any point in a stationary magnetic field is equal to the curl of the magnetic induced field intensity at the same point.

The volume densities of electricity and magnetism are expressed by the equations

$$(A_s) \qquad \text{div } \mathbf{A} = E, \qquad (B_s) \qquad \text{div } \mathbf{B} = M.$$

According to these equations, the divergence of the electric or the magnetic actual flux at any point represents the amount of electricity or of magnetism per unit volume at the same point. The latter quantity is fictitious, since true magnetism is unknown.

We have next to notice the equations which define the electric and magnetic properties of the free ether. They are

$$(A_{4}) \begin{array}{c} (1) & \alpha = \alpha_{0}, \\ (2) & E = 0, \\ (3) & \mathbf{i} = 0, \\ (4) & \mathbf{A}_{e} = 0, \end{array} \begin{array}{c} (1) & \beta = \beta_{0} \\ (2) & M = 0, \\ (3) & \mathbf{j} = 0, \\ (4) & \mathbf{B}_{e} = 0. \end{array}$$

### 8. Dynamical Properties of the Electric and Magnetic Field.

From the investigations of Heaviside it appears that the probable forms of expression for the mechanical forces exerted by an electromagnetic system against the exterior agencies acting upon it are, when reckoned per unit volume,

$$(A_{s}) \qquad \mathbf{f}_{e}' = \mathbf{a}_{a} \operatorname{div} \mathbf{A} - \frac{1}{2} \mathbf{a}_{a}^{2} \nabla \alpha + (\operatorname{curl} \mathbf{a}_{a}) \times \mathbf{A},$$

$$(B_{\mathfrak{z}}) \qquad \mathbf{f}_{\mathfrak{m}}' = \mathbf{b}_{\mathfrak{z}} \operatorname{div} \mathbf{B} - \frac{1}{2} \mathbf{b}_{\mathfrak{z}}^{2} \nabla \beta + (\operatorname{curl} \mathbf{b}_{\mathfrak{z}}) \times \mathbf{B},$$

due to the electric and magnetic field respectively. As these equations are identical in form, it will suffice to give the interpretation of the latter.

The first term on the right represents that part of the force which is due to true magnetism, and is probably fictitious since distributions of true magnetism are unknown. If such a force existed, it would be in magnitude equal to the product of the magnetic field intensity into the volume density of true magnetism; and it would have the direction of the magnetic field intensity. The second term represents that part of the force which is due to heterogeneity of the medium and has the direction of the gradient of the magnetic inductivity. Since the magnetic energy per unit volume is  $\frac{1}{2}\beta b_a^2$ , the magnitude of this force is the magnetic energy per unit volume multiplied by the ratio of the inductivity gradient to the inductivity itself. The force represented by the last term may be split into two distinct parts. For

$$\begin{aligned} & \operatorname{curl} \, \mathbf{b}_a = \operatorname{curl} \, \mathbf{b} + \operatorname{curl} \, \mathbf{b}_e, \\ & \text{and hence} \\ & (\operatorname{curl} \, \mathbf{b}_a) \times \mathbf{B} = (\operatorname{curl} \, \mathbf{b}) \times \mathbf{B} + (\operatorname{curl} \, \mathbf{b}_e) \times \mathbf{B}. \end{aligned}$$

Now curl **b** represents the *true* electric current density, and the term (curl **b**)  $\times$  **B** expresses the force due to the existence of *true* electric current. In magnitude it is equal to the product of the

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magnitude of the *true* current density and the magnetic flux multiplied by the sine of the angle between the directions of these quantities; its line of action is perpendicular to the current and the magnetic flux and its direction is indicated by any one of the familiar rules. The term (curl  $\mathbf{b}_{o}$ ) × B represents the force due to permanent magnetization, curl  $\mathbf{b}_{o}$  being the fictitious current density which is employed on Ampere's theory in representing permanent magnetization. The magnitude and direction of this force are found as in the case for the force upon the true current.

By integration of equations  $(A_s)$  and  $(B_s)$  the expressions for the resultant forces upon an electrified or magnetized body in an electromagnetic field may be obtained. In this way we get, for the electric and the magnetic case respectively,

$$\begin{array}{ll} (A_6) \quad \mathbf{F}_a' = \int \mathbf{a}_a \ \mathrm{div} \ \mathbf{A} d\tau - \int \frac{1}{2} \mathbf{a}_a^2 \nabla u d\tau + \int (\mathrm{curl} \ \mathbf{a}_a) \times \mathbf{A} d\tau, \\ (B_6) \quad \mathbf{F}_m' = \int \mathbf{b}_a \ \mathrm{div} \ \mathbf{B} d\tau - \int \frac{1}{2} \mathbf{b}_a^2 \nabla_i \beta d\tau + \int (\mathrm{curl} \ \mathbf{b}_a) \times \mathbf{B} d\tau, \end{array}$$

the integrations extending throughout the whole body.

## Specifications which Uniquely Determine the Electric and Magnetic Fields.

As is well known, a theorem analogous to that given in section (6) for the hydrodynamic field holds for the case of the stationary electric or the stationary magnetic field. Thus:

The electric field is uniquely determined when the distributions of the divergence of the actual electric flux, of the curl of the electric induced field intensity, and of the electric energetic flux, are given; and a similar statement holds for the magnetic field.

### IV. ESTABLISHMENT OF THE CHANGE-OF-STATE ANALOGY.

In discussing the properties of the hydrodynamic system consisting of the *fluid bodies* and the *fundamental fluid*, we have made constant use of two fundamental vector quantities, viz., the velocity of the fluid and the specific momentum of the fluid. In order to reach the proper forms for the expressions giving the geometrical and dynamical properties of the fluid system, with reference to the analogy with the stationary electric or magnetic field, each of these two fundamental vectors has been considered as made up of two others, the induced and energetic vectors. Six vector quantities in all have been employed, but only two of these are independent, as a glance at the equations of connection  $(C_1)$  will show. A knowledge of the distributions of any two of these six vectors is sufficient to characterize the state of the fluid system so far as its geometry is concerned. The dynamical properties of the fluid motion are to be inferred from the equation  $(C_b)$ .

We have now to show that an analogy exists between the equations expressing the geometrical and dynamical properties of the hydrodynamic field and the equations defining the geometrical and dynamical properties of *either* the stationary electric field *or* the stationary magnetic field.

In establishing the analogies a table (Table III.) giving the scheme of correspondence of quantities and things will first be given, and then the justification of the scheme will be given. The notation employed to designate the various quantities is also given in Table III.

Electric.	Hydrodynamic.	Magnetic.		
The ether,	The fundamental fluid,	The ether.		
Electrified bodies,	The fluid bodies,	Magnetized bodies.		
Inductivity (a),	Density of fluid $(\gamma)$ ,	Inductivity $(\beta)$ .		
Flux (A),	Specific momentum (C),	Flux (B).		
Induced flux $(\mathbf{A}_i)$ ,	Induced sp. momentum $(C_i)$ ,	Induced flux (Bi).		
Energetic flux (A.),	Energetic sp. momentum $(C_e)$ ,	Energetic flux (B <sub>e</sub> ).		
Field intensity (a,),	Velocity (Ca),	Field intensity (b.).		
Induced field intensity (a),	Induced velocity (c),	Induced field intensity (b).		
Energetic field intensity (a.),	Energetic velocity (c,)	Energetic field intensity (b.).		
Volume density of electric- ity $(E)$ ,	Local time rate of decrease of density (H),	Volume density of magnet- ism (M).		
Current density (j),	Kinematic vortex density (k),	Current density (1).		

TABLE III.

SCHEME OF CORRESPONDENCE AND NOTATION.

The justification of the scheme of correspondence given in Table III. is to be found through comparison of the equations which express the properties of the hydrodynamic field of the change-of-state analogy with the corresponding equations of the stationary electric or magnetic field. We will collect and rewrite the equations which are to be compared.

The equations of connection, which give the relations among the actual, induced and energetic vectors, are :

ELECTRIC. HYDRODYNAMIC. MAGNETIC.  $\mathbf{A} = \mathbf{A}_{i} + \mathbf{A}_{o}, \qquad \mathbf{C} = \mathbf{C}_{i} + \mathbf{C}_{o}, \qquad \mathbf{B} = \mathbf{B}_{i} + \mathbf{B}_{o},$   $(A_{1}) \qquad \mathbf{A}_{i} = \alpha \mathbf{a}, \qquad (C_{1}) \qquad \mathbf{C}_{i} = \gamma \mathbf{C}, \qquad (B_{1}) \qquad \mathbf{B}_{i} = \beta \mathbf{b},$   $\mathbf{A}_{e} = \alpha \mathbf{a}_{e}, \qquad \mathbf{C}_{e} = \gamma \mathbf{C}_{e}, \qquad \mathbf{B}_{e} = \beta \mathbf{b}_{e}.$ 

The equations which give the densities of the magnetic (fictitious) and the electric conduction currents, and the kinematic vortex density are :

ELECTRIC. HYDRODYNAMIC. MAGNETIC.  $(A_2)$  curl  $\mathbf{a} = -i$ ,  $(C_2)$  curl  $\mathbf{c} = -\mathbf{k}$ ,  $(B_2)$  curl  $\mathbf{b} = \mathbf{j}$ .

The equations which give the volume densities of true electricity, of true magnetism (fictitious), and the rate of decrease of the density of the fluid at any point are :

ELECTRIC. HYDRODYNAMIC. MAGNETIC.  $(A_3)$  div  $\mathbf{A} = E$ ,  $(C_3)$  div  $\mathbf{C} = H$ ,  $(B_3)$  div  $\mathbf{B} = M$ .

The equations giving the properties of the free ether, and of the fundamental fluid are :

ELECTRIC.  

$$a = a_0,$$
  $\gamma = \gamma_0,$   $\beta = \beta_0,$   
 $(A_i)$   
 $i = 0,$   $(C_i)$   
 $\mathbf{k} = 0,$   $(B_i)$   
 $\mathbf{k} = 0,$   $\mathbf{k} = 0,$   $\mathbf{k} = 0,$   $\mathbf{k} = 0,$   
 $\mathbf{A}_e = 0,$   $\mathbf{C}_e = 0,$   $\mathbf{B}_e = 0.$ 

The equations summarized above give the geometrical properties of the vectors which characterize the three types of fields.

The dynamical correspondence is established by referring to the

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HYDRODYNAMIC.

$$(C_{\mathfrak{s}}) \qquad \mathbf{f}_{\mathfrak{s}}' = -\mathbf{c}_{\mathfrak{s}} \operatorname{div} \mathbf{C} + \frac{1}{2} \mathbf{c}_{\mathfrak{s}}^{2} \nabla \gamma - (\operatorname{curl} \mathbf{c}_{\mathfrak{s}}) \times \mathbf{C},$$

MAGNETIC.

$$(B_{\mathfrak{z}}) \qquad \mathbf{f}_{\mathfrak{m}}' = \mathbf{b}_{\mathfrak{a}} \operatorname{div} \mathbf{B} - \frac{1}{2} \mathbf{b}_{\mathfrak{a}}^{2} \nabla_{\beta} + (\operatorname{curl} \mathbf{b}_{\mathfrak{a}}) \times \mathbf{B}.$$

The three fields are severally uniquely determined when the distributions of the following quantities are given in the three cases:

ELECTRIC.	HYDRODYNAMIC.	MAGNETIC.
div <b>A</b> ,	div C,	div <b>B</b> ,
curl <b>a</b> ,	curl <b>c</b> ,	curl <b>b</b> ,
<b>A</b> ,	C <sub>e</sub> ,	<b>B</b>

An inspection of the equations summarized above shows the degree of completeness of the analogy. It is quite complete except for the reversed algebraic signs in the expression for the force per unit volume in the hydrodynamic field, when compared with the corresponding expressions for the force in the electric or magnetic fields.

V. DISCUSSION OF THE ANALOGY.

The analogy which has been established shows that the vectors which are employed to describe the properties of the hydrodynamic field are geometrically related in the same way as the vectors which are used to describe the stationary electric or the stationary magnetic field. As far as the geometrical relationship of corresponding vectors is concerned the analogy is quite complete. The dynamical aspects of the analogy bring out a curious and interesting result; for, as we have just seen, the forces in the hydrodynamic field, although of the proper form, are oppositely directed to the corresponding forces in the electric or magnetic field. The same curious departure is present in the Bjerknes form of the analogy. magnetic field has just the same claim to completeness as that found in the change-of-state analogy. But owing to the fact that the *fluid bodies* in the Bjerknes form of the analogy always consist of the same particles of fluid, they must, in general, as time goes on necessarily change in form and in position in space.

If one attempts to make the *fluid bodies* in the Bjerknes form of the analogy persist in a fixed geometrical configuration, he may (following Professor Bjerknes) introduce the necessary conditions to insure a stationary state of motion of the fluid. This procedure, however, limits very much the generality of the motion, inasmuch as the possibility of motion normal to the surface of a *fluid body* is thereby excluded. The scope of the analogy is consequently much restricted.

With the same object in view Professor Bjerknes has also assumed a vibratory motion of the fluid, so that the *fluid bodies* shall execute small vibrations about invariable mean positions in space and thus *appear* to remain stationary. Here again a notable restriction upon the generality of the motion and upon the scope of the analogy is introduced. For in the Bjerknes form of the analogy the dynamic vortex density must be conserved at all points of the fluid, but this is the quantity which corresponds to electric, or magnetic, current density, and in a vibratory state of motion it is evident that it must vanish everywhere, since it cannot be varied. The hydrodynamic equations then reduce to those corresponding to *static* electric or magnetic fields with consequent loss of generality.

In the next section will be given the investigations of the conditions which have to be satisfied if the change-of-state analogy is to persist as time goes on. It will appear that no real loss in generality is involved through the introduction of these conditions; and that therefore the change-of-state analogy will persist in time and will hold for stationary as well as static electric or magnetic fields.

### 9. Conditions for the Persistence of the Analogy.

We have already seen that the state of motion in the hydrodynamic system is completely specified when the distributions of

## C, curl c, and div C

are given. Now in the stationary or steady state in the electric or

magnetic system the corresponding quantities are invariable with time; and if the analogy is to persist with time, it is necessary in the hydrodynamic case that

$$\frac{\partial \mathbf{C}}{\partial t} = 0,$$
$$\frac{\partial (\operatorname{curl} \mathbf{c})}{\partial t} = 0,$$
$$\frac{\partial (\operatorname{div} \mathbf{C})}{\partial t} = 0.$$

The condition has already been imposed (eq. (9)) that the energetic specific momentum shall be locally conserved; hence the first of these conditions must always be satisfied. The second condition requires that the curl of the induced velocity shall be locally conserved, or in other words that the density of the kinematic vortex shall be invariable with time. There is obviously no objection to imposing this condition. The third condition requires the local conservation of div C or, on account of the equation of continuity, (2), that  $\partial r/\partial t$  shall be constant with respect to the time. Owing to the introduction of this condition some difficulty of interpretation appears. For at points where  $\partial r/\partial t$  has other than zero value, we have to conceive the density as always increasing or always decreasing. If it be supposed that the initial density at such points is so great that finite variations of its value may be neglected, the difficulty disappears. Or, we may restrict the analogy, so that it applies to those electric and magnetic systems only which have no distribution of true electricity or magnetism. In the case of the magnetic field we have reason to believe that true magnetism does not exist. In the light of the difficulty just discussed it would appear that the analogy more appropriately applies to the stationary magnetic field.

The difficulty might also be overcome through the introduction of a state of vibratory motion into the fluid system, in a manner similar to that used by Professor V. Bjerknes, and referred to above. But this procedure has the disadvantage that the analogy is thereby restricted to static electric and magnetic fields.

Apart from the difficulty just discussed, there is nothing against

the introduction of the conditions for a steady state of motion in the hydrodynamic system, in order that the analogy shall persist with lapse of time. Perhaps the most characteristic feature of the change-of-state analogy is that which permits of the introduction of the conditions for a steady state of motion in the fluid system without requiring the motion normal to the surface of a *fluid body* to vanish, with the consequent loss of generality in the analogy.

### VI. ANOTHER POSSIBLE FORM OF THE ANALOGY.

Another form of the change-of-state analogy may be obtained by adopting a different mode of development of the hydrodynamic equation of motion than that given in detail above. It does not appear, however, to furnish an analogy which is any broader than the one already dealt with. For this reason it will suffice to refer briefly to its principal features only, omitting the steps in the mathematical development. The correspondence of quantities is the same as in the first form of the analogy.

Following a process very similar in many respects to that employed in developing the equation of motion in the first form of the analogy, it appears that the hydrodynamic equation of motion,

(1) 
$$\gamma \frac{d\mathbf{c}_a}{dt} = \mathbf{f} - \nabla p,$$

may be written in the form

$$(4') \quad \frac{\partial \mathbf{C}_i}{\partial t} + \nabla (\frac{1}{2}\gamma \mathbf{c}^2 + \mathbf{C}_{\bullet} \cdot \mathbf{c}) - \frac{1}{2}\mathbf{c}^2 \nabla \gamma + (\operatorname{div} \mathbf{C})\mathbf{c} + (\operatorname{curl} \mathbf{c}) \times \mathbf{C} - \mathbf{c}\mathbf{C}_{\bullet} \nabla = \mathbf{f} - \nabla p.$$

The induced specific momentum is now required to satisfy the condition

(5') 
$$\frac{\partial \mathbf{C}_i}{\partial t} = -\nabla(p + \frac{1}{2}r\mathbf{c}^2 + \mathbf{C}_s \cdot \mathbf{c}),$$

and the energetic velocity must then satisfy the equation

(6') 
$$\gamma \frac{d\mathbf{c}}{dt} = \mathbf{f} - \mathbf{c} (\operatorname{div} \mathbf{C}) + \frac{1}{2}\mathbf{c}^2 \nabla \gamma - (\operatorname{curl} \mathbf{c}) \times \mathbf{C} + \mathbf{c}\mathbf{C} \nabla.$$

From equation (5') it is easily proved that the dynamic vortex density must be conserved. Furthermore it may readily be shown that the geometrical properties expressed by the equations  $(C_1) \cdots (C_4)$  are also characteristic of the second form of the analogy.

In order to arrive at the dynamic analogy the condition that the energetic velocity of every fluid particle be conserved is introduced, so that

$$(9') \qquad \qquad \frac{d\mathbf{c}_{\bullet}}{dt} = \mathbf{0}.$$

This equation should be compared with equation (9), the corresponding one in the first form of the analogy.

The introduction of the condition (9') leads to the following expression for the elementary force exerted per unit volume of fluid against exterior agencies:

$$(C_s') \quad \mathbf{f}_{\mathbf{k}}'' = -\mathbf{c} (\operatorname{div} \mathbf{C}) + \frac{1}{2} \mathbf{C}^s \nabla \gamma - (\operatorname{curl} \mathbf{c}) \times \mathbf{C} + \mathbf{c} \mathbf{C}_s \nabla \mathbf{c}$$

This equation should be compared with equation  $(C_{\delta})$ . It will be noticed that the expression for the elementary force in equation  $(C_{\delta}')$ does not correspond in form to the corresponding expressions for the electric or magnetic field as given by Heaviside, and expressed in equations  $(A_{\delta})$  and  $(B_{\delta})$ . Granted that the equations of Heaviside referred to are the correct ones, it is evident that the first form of the analogy is much to be preferred. It is only just to remark, however, that the same form of expression for the resultant force acting upon a *fluid body* is obtained through volume integration of the equation  $(C_{\delta}')$ , as that obtained from equation  $(C_{\delta})$  by the same process.

The first form of the analogy possesses some advantages over the second when the conditions for a steady state of motion are introduced, arising from the difference in the conditions (9) and (9').

Professor Bjerknes has shown in his lectures delivered at Columbia University that, with the correspondence of quantities which he assumes, there are at least two possible forms of the analogy. The first of these formally corresponds to the first form of the changeof-state analogy; and the second to the second form of the changeof-state analogy, outlined above.

### SUMMARY.

The object of the foregoing paper is to present the main features of a new form of a hydrodynamic analogy with the stationary electric or magnetic field.

The analogy developed is termed the change-of-state analogy, and is a modification of the well-known Bjerknes analogy. For this reason there is given at the beginning of the paper a short account of the principal features of the Bjerknes analogy. A general description of the hydrodynamic system employed in the change-of-state analogy is then given. The differences in the two forms of analogies arise, primarily, from the different correspondence of the hydrodynamic with the electric or magnetic quantities which is assumed.

The correspondence of quantities which is assumed in the changeof-state is the following :

HYDRODYNAMIC.	ELECTRIC OR MAGNETIC.
Velocity	Field Intensity
Specific momentum	Flux
Density	Inductivity.

In the Bjerknes form of the analogy velocity corresponds to flux, specific momentum to field intensity, and specific volume to inductivity.

The hydrodynamic system of the change-of-state analogy consists of a *fundamental fluid* of infinite extent, within which there are certain fixed regions, called *fluid bodics*. The density of the *fundamental fluid* is supposed to be constant both in time and space. The fluid in a *fluid body* may be compressible, and the density variable from point to point. In both cases a perfect fluid is assumed.

The chief distinguishing feature of the fluid system is to be found in the conditions which allow a fluid body to remain fixed in space and yet permit of motion of the fluid, both within and without, normal to its surface. Thus the *fundamental fluid* may enter the region of a fluid body, experiencing as it does so, however, a change of state, acquiring the density and properties of motion of the *fluid body*, and losing those of the fundamental fluid. In like manner, fluid may leave the region of a *fluid body*, at the same time acquiring the properties of the *fundamental fluid*, and losing those of the *fluid body*. This feature permits of the assumption of a steady state of motion of the fluid without serious loss of generality in the scope of the analogy.

A summary of the most important results found is given below:

1. The *fundamental fluid* may be consistently assigned properties which are analogous to those of the free ether.

2. The *fluid bodies* may be consistently assigned properties which are analogous to those of the stationary electric or the stationary magnetic field — with the exception that the mechanical forces to which they are subject are oppositely directed to the corresponding forces acting upon material bodies in the electric or magnetic field.

3. The geometrical relationships among the velocity and momentum vectors and the density of the fluid is expressed by a system of equations which are of the same type as the equations of Maxwell, expressing the relationships among the field-intensity and flux vectors and the inductivity in the stationary electric or the stationary magnetic field.

4. The mechanical force acting per unit volume of fluid is expressed in the form of an equation which is of the same type as the equation given by Heaviside, expressing the mechanical force acting per unit volume in the electric or magnetic field. This means, of course, that the resultant force acting upon a whole *fluid body* must correspond, except for the reversed sign, to the resultant force acting upon a material body in the electric or magnetic field.

5. The analogy established permits of the assignment of a steady state of motion to the hydrodynamic system; consequently the analogy is one which will persist with lapse of time, and without loss of generality. In this respect it possesses an advantage over the Bjerknes form of the analogy.

6. A second form of the change-of-state analogy is shown to be possible. The same correspondence of quantities is employed as in that to which the above results refer. The second form of the analogy leads to an expression for the mechanical force, acting per unit volume of the fluid, which is different from that found in the first form. It does not correspond therefore to the equation given by Heaviside for the corresponding case in the electric or magnetic field. But the expression for the *resultant* force upon a *fluid body* is the same as in the first form of the analogy, and therefore corresponds to the expression as given by Heaviside for the corresponding electric or magnetic case.

COLUMBIA UNIVERSITY, January, 1908.



# A MECHANICAL EFFECT ACCOMPANYING MAGNETIZATION.

BY O. W. RICHARDSON..

N the electron theory of matter the magnetic properties of bodies arise from the motion of the constituent electrons of their atoms. It is well known that all bodies may be divided according to their magnetic quality into three classes : (1) diamagnetic, (2) paramagnetic and (3) ferromagnetic. Bodies belong to the diamagnetic class if their atoms possess no resultant magnetic axis. They would also belong to this class even if they possessed a resultant magnetic axis provided this axis had no tendency to set in a definite direction in an external magnetic field. By the word atom in this discussion is meant a magnetic atom ; that is, the smallest portion of the matter under consideration whose electronic properties are such that the magnetic properties of the whole can be built up by the piling together suitably of similar particles. The facts appear to indicate that in many cases the magnetic atoms are the same as the chemical atoms, in other cases possibly not.

Paramagnetic and ferromagnetic substances both appear to result when the constituent atoms both possess a resultant magnetic axis and also set themselves in a definite direction under the influence of an external magnetic field. The difference between the two classes appears to depend on the relative magnitude of the atomic magnetic moment and the forces called into play by the displacement of the atoms. When the restoring forces of non-magnetic type due to a small displacement give rise to a couple which is great compared with that exerted by the external field on the equivalent atomic magnet, the magnetic fields at our disposal will only produce small rotations of the atoms and these small rotations will be proportional to the external magnetic field. For small rotations the *resultant* intensity of magnetization will be proportional to the rotation. Thus the intensity of magnetization will always be proportional to the magnetizing field over the range of values of the latter which are practicable; the body will thus be paramagnetic.

Ferromagnetic substances are those for which the restoring couples are not great compared with those of magnetic type. In this case we are able to apply external fields great enough to bring all the atomic magnets into line with the applied field. The body will then possess its maximum or "saturation" value of intensity of magnetization. For a fuller discussion of this aspect of the subject the reader is referred to a paper by Langevin.<sup>1</sup>

On this view it will be seen that the distinction between paramagnetic and ferromagnetic substances is one of degree only. It depends only on the magnitude of the restoring forces of non-magnetic type compared with the displacing forces of magnetic type. It might be possible for a substance which was in general paramagnetic to become ferromagnetic by combining it with some substance which increased the freedom of motion of its atoms. This may be the explanation of the peculiar behavior of the alloys of manganese investigated by Heusler. It is obvious that the converse case is also to be expected and may be applied to explain the behavior of some of the alloys of iron and the other ferromagnetic metals.

On the view that we have taken the resultant magnetic fields which the atoms of magnetic (as opposed to diamagnetic) substances possess, arise from the motion of their constituent electrons in closed orbits. If e is the charge in electromagnetic units carried by an electron describing an orbit possessing approximately circular symmetry and lying approximately in one plane, then if a is the area of the orbit and t the time in which it is described it can be shown that the value of the magnetic force, at any point whose distance is considerable compared with the dimensions of the orbit, averaged over a revolution is the same as that arising from a magnet of moment ea/t in electromagnetic units. The equivalent magnet passes through the center of the orbit and is normardicular to the plane of the latter sidered, of the magnetic moment of the element of volume dv, supposed to contain a large number of them, is  $nea_v/t \cdot dv$ .

If the azimuths of the different orbits differ then the average value of  $a_p$  must be taken in the above formula. In the case of an unmagnetized bar of iron one direction is as probable as another for the azimuth so that the average value of  $a_p$  is equal to zero.

If we proceed to calculate the intensity of magnetization induced in the substance by a uniform external field in the direction of z, taking account of the possible presence of both positive and negative electrons in motion, we find

$$M_{s} = NE \begin{bmatrix} A_{p} \\ T \end{bmatrix} + ne \begin{bmatrix} \overline{a}_{p} \\ t \end{bmatrix}.$$
(1)

where the bars denote average values. Here  $M_s$  is the magnetic movement per unit volume, and for the right hand side the capitals refer to the positive ions. In this formula the proper signs must be given to E and e and also to  $\overline{A_p}$  and  $\overline{a_p}$  according to the sign of the charge and the direction of rotation. If there are only rotating negative electrons present then  $M_s$  has the value given previously, namely,  $nea_p/t$ .

We shall now proceed to obtain an expression for the moment of momentum of the revolving electrons about the direction of the applied magnetic force. Let the line about which the moment of momentum is calculated be the axis of z so that it is given by the equations x = y = 0. Consider any approximately circular orbit, the coördinates of whose center are  $x_0 y_0 z_0$ . Let the coördinates of the revolving electron referred to this center at any instant be  $\xi$ ,  $\eta$ ,  $\zeta$ ; thus its coördinates referred to the point on the axis about which the moment of momentum is to be taken are  $x_0 + \xi$ ,  $y_0 + \eta$ ,  $z_0 + \zeta$ . These are the displacements of the particle, and its velocity components are  $d\xi/dt$ ,  $d\eta/dt$  and  $d\zeta/dt$ . The moment of momentum about the z-axis is thus

$$m\left(\overline{x_0+\xi}\,\frac{d\eta}{dt}-\overline{y_0+\eta}\,\frac{d\xi}{dt}\right)=m\left\{x_0\,\frac{d\eta}{dt}-y_0\,\frac{d\xi}{dt}+\xi\,\frac{d\eta}{dt}-\eta\,\frac{d\xi}{dt}\right\}.$$

Averaging this over a complete revolution evidently the mean values



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are

$$\overline{x_0 \frac{dr_i}{dt}} = 0, \quad \overline{y_0 \frac{d\xi}{dt}} = 0$$

and

$$\overline{\xi \frac{d\eta}{dt}} = -\overline{\eta \frac{d\xi}{dt}} = \frac{\text{area of projected orbit}}{t} = a_p/t.$$

Hence the average moment of momentum about any axis is independent of the position of that axis, so long as its direction is the same and is equal to  $2ma_{\mu}/t$ . If there are revolving electrons with both positive and negative charges we find, with the same convention as to signs as that already used, that  $U_{\mu}$  the moment of momentum per unit volume arising from the motion of the electrons is given by

$$U_{s} = 2 \left\{ NM \begin{bmatrix} A_{p} \\ T \end{bmatrix} + nm \begin{bmatrix} a_{p} \\ t \end{bmatrix} \right\}.$$
(2)

We may regard the formulæ (1) and (2) as embracing all the electrons in the atom whether moving or not. In this case since the body as a whole is uncharged we have NE = ne. The quantities  $A_p/T$  and  $a_p/t$  will represent the resolved areal velocities of all the positive and negative electrons respectively; we may write then for brevity A and a respectively. With this understanding

$$M_{a} = nea \left[ 1 + \frac{A}{a} \right]$$

and

$$U_{a} = 2nma \left[ 1 + \frac{e}{E} \frac{M}{m} \frac{A}{a} \right] = 2 \frac{m}{e} M_{a} \frac{1 + \frac{e}{E} \frac{M}{m} \frac{A}{a}}{1 + \frac{A}{a}}.$$
 (3)

For small fields A and a will both be proportional to the applied field so that A/a will be a constant independent of the field strength and depending only on the constitution of the atom. So that in every case the moment of momentum per unit volume will be proportional to the intensity of magnetization, the factor of proportionality depending only on the charges and masses of the electrons and their configuration in the atom.

The most usual form of the electron theory of matter assumes

that the negative electrons alone are in motion and most of the experimental facts seem to be in favor of this conclusion. In this case the above result acquires an important simplification. If the positive electrons are free from orbital motions A = 0 so that

$$U_{s} = 2 \frac{m}{e} M_{s}. \tag{4}$$

Thus the ratio between the moment of momentum per unit volume and the intensity of magnetization is the same for all substances and is equal to twice the inverse of the specific charge (e/m) of the negative electrons.

Experiments are at present in progress in the physical laboratory of Princeton University with the object of detecting the existence of this moment of momentum experimentally. Consider a long thin cylindrical bar of iron suspended by a fiber passing through its axis of figure so that it is capable of vibrating about a vertical axis. When the bar is not magnetized its constituent electrons will not possess a resultant moment of momentum about any axis as on the average one azimuth is as probable as another for the orbits. Now consider the effect of suddenly applying a vertical magnetic field. The movable orbits will set so as to leave a balance in favor of the plane perpendicular to the direction of the field. There will thus be created a moment of momentum about the axis of suspension. But by the laws of dynamics the total moment of momentum of any selfcontained system is invariable. The moment of momentum acquired by the revolving electrons must thus be balanced by an equal reaction elsewhere. It would appear that this reaction is to be sought for in one of two places. The most reasonable I think is to suppose that it is effective on the rest of the atom, the part which is not revolving in an orbit. In this case it would be made evident by a twisting of the suspended system as a whole. The twist would of course be purely temporary owing to the restoring effect of the

moment of momentum is proportional to the mass of the revolving particles and independent of their charges (except in so far as their mass is electromagnetic).

Assuming that the magnetism of iron is due solely to the motion of negative electrons the torsional reaction should easily give a measurable effect. If any appreciable portion of the magnetization were to arise from the motion of heavier charges the effect would be proportionately greater. It will be seen that this method forms a valuable addition to our present equipment for investigating magnetic phenomena. So far experimental success has not been attained owing to the difficulty of eliminating disturbing effects.

PRINCETON, N. J.,

December 23, 1907.

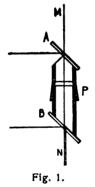


### A NEW TYPE OF SEXTANT.

By L. A. FREUDENBERGER.

THE ordinary sextant (Hadley's) makes use of the well known law of reflection — that the reflected and incident rays make equal angles with the normal to the mirror surface — in order to obtain a movement of a vernier arm of half the angle measured. The arc is graduated, however, to read the angle directly.

In the new type of sextant devised by the writer, the law of reflection, that the incident and reflected ray lie in the same plane, normal to the mirror surface, is taken advantage of to make the angular movement of the vernier-arm equal to the angle measured. The principle of the new type of sextant is substantially shown by Fig. 1.



A is a full silvered mirror, mounted with adjusting screws to make an angle of  $45^{\circ}$  with the axis MNof the instrument. The mirror A rotates in the cone bearing P about the line of sight MN as an axis. A vernier-arm C (not shown in Fig. 1) is fastened to the frame of A and moves over a graduated arc fastened to the frame of B, serving to measure the angle of rotation of the mirror A around MN as an axis. B is a half silvered mirror mounted with adjusting screws to make an angle of  $45^{\circ}$  with the axis MN. In Fig. 1 the positions of the mirrors are shown for parallel rays (both mirrors reflecting

an image of the horizon, which two images are brought in coincidence for the "zero" setting). If mirror B is kept sighted on the horizon, it is evident that with the sun at the meridian, mirror Awill have to be rotated 90° about the axis MN in order to reflect the sun's image down the line of sight.

Figures 2 and 3 are photographs giving front and rear views of a sextant embodying the above principles, constructed by the writer, and in which the mirrors and accessories are clearly shown.



In the practical use of a sextant — sighting on the sun and the horizon, for instance — accuracy is limited by the difficulty the eye

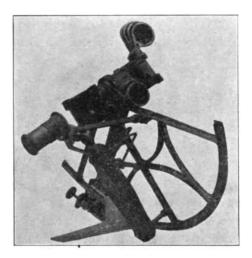


Fig. 2.

experiences in deciding when the sun's disc just touches the horizon. In the Hadley sextant, suppose that the eye can determine the

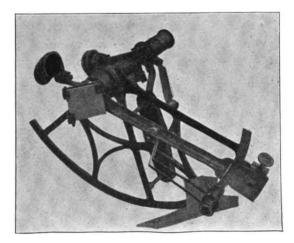


Fig. 3.

coincidence of two images to within one minute of angular movement of the mirror surfaces. This means that the actual angle between the two objects can only be determined within two minutes of angular measure. In the new type of sextant (Fig. 1), let the coincidence of two images be determinable again within one minute of angular movement of the mirror A in Fig. 1. This means that the actual angle between the two objects can also be determined within a minute of angular measure. This possibility of increasing the accuracy of measurement is, of course, the sole advantage of the new type of sextant. The new type of sextant differs from the old in the following particulars :

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The field of view in the new type of sextant appears precisely the same as in the Hadley type, except that in driving forward the vernier-arm the moving field of view travels through a vertical arc of a circle, while the moving field of view in the Hadley sextant makes a straight vertical movement.

In locating two objects (see Fig. 2), so as to make them appear in the field of view, the line of sight of the telescope is at right angles to the plane containing the two objects and the observer, *i. e.*, the plane of the graduated arc of the instrument passes through the two objects. Vertical movements of the field of view are obtained by rotating the instrument as a whole about the line of sight of the telescope.

The Hadley type of sextant usually measures actual angles to 120° of arc or more. Since the angular movement of the mirror is only half this the sector of the graduated arc is only 60°, though graduated to read 120° directly. To secure an angular measurement of 120° in the new type of sextant, it is necessary to have a graduated sector of 120 actual degrees. Strictly speaking, the new instrument can hardly be called a sextant, since the graduated sector subtends one third of a circle instead of one sixth.

The adjustments of the mirrors in the new type of sextant can be accomplished most easily at sea where a horizon is always available.

To adjust for "zero" reading, the movable vernier-arm is clamped at the zero reading of the graduated arc. Mirror A (Fig. 1) is then adjusted until the two images of a very distant object appear straight line (the horizon for instance), want of proper adjustment of mirror B would be shown by the two horizon lines, though meeting for the "zero" reading, not forming a continuous unbroken line but being bent at the line of division of the half silvered mirror. If desirable, the graduations and arc may be extended to  $180^{\circ}$  or even to  $360^{\circ}$ , when the adjustment of the mirrors may be exact, since the two horizon lines should coincide when the vernier-arm is set at  $0^{\circ}$  and also when set at  $180^{\circ}$ . An angle and its supplement might thus be measured, in order to compensate for eccentricity errors of the graduated arc.

Delaware College, Newark, Delaware



### PROCEEDINGS

### OF THE

# American Physical Society.

# UPON THE MAGNETIC SEPARATION OF THE SPECTRAL LINES OF BARIUM, YTTRIUM, ZIRCONIUM AND OSMIUM.<sup>1</sup>

#### BY B. E. MOORE.

**PRESTON**<sup>3</sup> observed a similarity in the magnetic separation for spectral lines which formed similar series. Runge and Paschen<sup>3</sup> confirmed this observation for a number of substances. The inverse process would be to make use of the magnetic separation to investigate for series in substances where no such relationship has as yet been discovered. Runge used this method in barium, and found types of separation belonging to well-established series but not enough representatives to make a series. The present experiment proposes to use this inverse method in a more extended study of barium and other substances in which series have not been found.

The substances were volitilized in the usual way, by means of the spark in a strong magnetic field (24,400 cgs. units per sq. cm.) and photographed by means of a 21 ft. grating. The components parallel and perpendicular respectively to the lines of force were separated by a calcite prism. In barium there were observed three quadruplets of two different types, 4 sextets of three types, two octets of two types, 32 triplets which group themselves into four types and 21 triplets of various separations but generally represented in magnitude in some line having more than three components. The yttrium lines may be designated as follows: Two lines have 12 components each but are unlike; five lines have 9 components each but no duplicates; two lines have 8 components each, but two types; three lines are sextets, and two are duplicates; there are two dissimilar quintets; there are 14 quadruplets and possibly one duplication: there are 74 triplets whose separations do not collect

Table of Intervals.

Interval or Ap Part of 'a	prox.	Multiples of the Intervals, Factors,	Number of Lines Represented.	Substance to which Types Belong.	Remarks.	λ
		22, 15, 12, 7	1	Zr		3459.1
		22, 16, 10, 9	1	Zr		4440.8
.10		13, 7	1	Zr		3891.61
$\left(\frac{a}{11}\right)$		15, 13, 11, 2, 0	1	Ne		
(11)		20,16,14,12,8,8,4 12, 7	1	Hg	1, NII 4	3655
		-	1	Os		4420.63
.12 (a/9) <sup>2</sup>		7, 4	1	Y		5510.1
a	18	7, 5, 4, 3, 2	1	Y		4235.89
6 1 .1	185	10, 9, 8, 7, 6, 2, 1, 0	1	Ne		
- ( .1	L9	14, 9, 5, 4, 0	1	Ne		
		9, 7, 5, 2, 0	1	Y		4398.21
.2	20	9, 6, 4, 3	1	Y		4083.89
		7, 6	1	Y		4682.5
2a/11		5, 1	1	Y		4375.11
		5, 2	1	Y		4177.68
		5, 4	1	Zr		4004.51
		10, 8, 7, 6, 4, 2	1	Hg		
.2	1	3, 2	1	Zr		3674.98
.2	2	9, 7, 3, 1	1	Y		4236.10
		4, 3	1	Zr		3894.00
a/5		4, 1	1	Zr		3916.16
		8, 7, 6, 5, 2, 1	1	Ne		
		8, 5, 4, 3		CuAg	I. N. S.	
				Al Tl		
		8, 5, 4, 3	1	Ba	I. N. S. <sup>1</sup>	
•		8, 4		Cu Ra	I. N. S. <sup>1</sup>	
				Ag Tl		
.25	ſ	6, 5, 1, 0	1	Zr		4171.65
$\frac{26}{2a}$	J	6, 1	1	Zr	$3a \div 11^{1,5}$	4256.66
$.26\left(\frac{2a}{9}\right)$ ?	l	6, 5, 3, 0	1	Zr	$\frac{a}{11}$ (15, 14, 8, 0)	4258.31
$(3a)^3$		8, 3, 2	3	Zr	$a \div 11 (21, 8, 5)$	See Zr 6 Comp
$\begin{pmatrix} 3a\\ 13 \end{pmatrix}^2$		7, 2, 0	1	Zr	$a \div 11 (21, 3, 5)$ $a \div 11 (18, 5, 0)$	4061.70
$\frac{a}{4}$ $\begin{cases} .2a}{2a}$	65	8, 5, 3, 2, 0	1	Y	· · - / - /	3584.71
4 .2	7	6, 5	1	Zr	a + 10 (16, 13)	3470.10
		6, 5, 4, 1, 0	1	Ne	• • •	
		7, 5, 4, 3	2	Zr	See Zr 8 Comp.	
	!	3, 2	1	Zr	•	4456.50

Interval or A Part of '	a.	Multiples of the Intervals, Factors,	Number of Lines Represented.	Substance to which Types Belong.	Remarks.	À
	.29	7, 1 2, 1	2	Zr Zr	$\lambda = 4003.28$ and	3578.40 3588.15
$\frac{3a}{11}$	.30	5, 2 (?) 4, 1 4, 1 4, 3	1 1 1 1	Ba Y Zr Zr		5971.9 3833.10 3890.58 3568.32
	.305	6, 3, 2, 0	1	Zr	a + 11(18, 9, 7, 0)	4093.32
ſ	.32	9, 4, 0 5, 2	1	Zr Zr		4187.30 4418.80
3 <i>a</i> 10	.33	4, 2 4, 1 2, 1	1 1 1	Zr Zr Zr		4034.30 4031.57 3284.89
l	.34	3, 2, 1 4, 1	1	Zr Zr		3396.51 3634.33
ſ	.36	5, 3, 1 3, 2, 2 5, 3, 1 4, 2	1 1 2 2	Zr Zr Ba Ba	4 ∫H and 2N \$	3483.70 3482.96
a 3	.37	4, 2 3, 1, 0 6, 4, 3, 2, 1, 0	1 1 2	-Y Zr Zr	See Zr 11 Comp.	3200.44 3376.42
l	.38	5, 3, 1 5, 1, 0 4, 1, 0	1 1 1	Zr Y Y		3323.21 4477.1 3951.76
$\left(\frac{4a}{11}\right)$	.39	4, 3, 2 4, 3	1 1	Zr Zr		4110.29 3434.08
$\left(\begin{array}{c} 11 \end{array}\right)$ $\left. \frac{3a}{8} \right\}$	.42	4, 3, 2, 1 (0?) 3, 2 3, 1 4, 1 4, 2 2, 1	8 6 3 2 1	Hg Zr Zr Zr Zr Zr Zr Zr	INII. h. See Zircon Quad- ruplet Table.	3125.8
l	.43	5, 4, 2, 1, 0 4, 3, 2, 0 6, 4, 1 4, 3, 2, 2, 1, 1	2 1 1	Zr Zr Zr Y	See Zr 9 Comp. a - 19 (27, 17, 4)	3368.01 3554.31 3818.49
	.48	<b>4</b> , <i>3</i> , <i>2</i> , <i>2</i> , <i>1</i> , <i>1</i> <b>3</b> , 1, 0	1	Zr		5350.5

Table of Intervals. -- Continued.

Interval Part	of Approx. t of ' <i>a</i> .'	Multiples of the Intervals. Factors.	Number of Lines Represented.	Substance to which Types Belong.	Remarks.	λ
<u>5a</u>	.50	5, 3 (1?) 3, 1 3, 2, 1, 1, 0 3, 1	1 3 1 2	Zr Zr Y Y	See Zr 4 Comp. 4 See Y Quadruplet.	3498.00 3950.51
[	.51	2, 1 3, 1 3, 2 (?)	1 2 1 1	r Zr Zr Zr	$\lambda = 4429.28$ and	4582.50 4024.20 3480.59
ſ	.53	2, 1, 1, 0	1	Zr		4055.2
	.54	5, 3, 2, 1, 0 4, 2, 2, 0, 0	111	Y Zr	I. N. I. S.	4199.46 4268.22
	.55	3, 2, 1 3, 2, 1 2, 1	1 2 1	Ba Y Y	$\lambda ==$ <b>4358.91</b> and	3195.80
		3, 2, 1 5, 3, 2	1	Zr Zr		4590.81 4431.70
		4, 3, 2, 1, 0 5, 3, 2, 1, 0 5, 2, 1, 0 4, 3, 2, 1 4, 3, 1 4	1	Ne Hg Hg Hg Hg Hg	I. N. I. S. I. N. II. S. 2NI 2NII 2NII	
l	.57	2, 1	2	Zr	$\lambda = 3934.99$ and	3973.68
6a +	.60 11	3, 2, 2, 0 1, 2	1	Zr Zr		4214.05 3454.71
	.63	3, 2, 1, 1, 0	1	Y		3628.89
3a/5	.67	3, 1, 0	1	Zr	$a \div 11(20, 7, 0)$	3501.50
<u>(3a/4</u>	)83	2, 1, 0	1	Zr		4046.30

Table of Intervals.-Continued.

In zirconium, two lines have eleven components each and are duplicates, two lines have nine components and are duplicates, six lines have

<sup>1</sup> Ba 4166 is just as accurately represented by a/4(6, 4, 3, 8) and Ra 4436, by a/4(6, 3). Neither of the two systems represents it accurately. Multiples of (a/11) represent these lines even better, except for one component.

<sup>2</sup> Series types, shown by Na, Cu, Ag, Al, Pt, Mg, Ca, Sr, Ba.

<sup>8</sup> The *p*-component lies outside of the *s*-component.

<sup>4</sup> When p- and s-components are duplicates in position, they are designated by repeating a number.

<sup>b</sup> The triplets of this first subordinate series are 3 and 5 times a/5.

eight components and two are duplicates, seven lines have seven components and all different types, sixteen lines have six components and not a duplicate, eleven lines have five components and likewise no duplicates, eighty lines are quadruplets. There are eight similar lines, when these are considered with reference to intensity. They subdivide into three groups, but even overlooking this no series could be found in these lines. There are six other lines of like separation but are irregularly distributed and therefore form no series. Four hundred and ten lines in zirconium are triplets. These lines have a wave retardation varying from  $\pm .33$ to  $\pm 2.75$  per cm. Near these extremes there are few lines but the separations like the vttrium triplets do not collect in specific groups as was found in barium. Twenty-nine lines in zirconium do not show separation. Most of these lines are probably other types whose separation is too small, too weak or too diffused to be observed. In osmium one quadruplet and 31 triplets showed upon the photographic plates. In their irregularity the triplets of osmium behave like yttrium and zircon.

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In comparing these lines with four or more components it became apparent that, although there were few duplicates, the magnitudes of separation were frequently repeated and that the separations of some lines could be picked out by taking one component from one line and another component from another line, etc. Combining some of these components together to form an ideal line with all components, it showed that these separations were nearly multiples of a smaller separation. This smallest distance between the components is designated the "interval," and the simple numbers by which they must be multiplied to produce the given separation the "factors." It was then found that the "intervals" were rather small in number for the substances studied and that the great variety in types arose from the variation in the "factors."

While engaged in this comparison an article appeared by Runge<sup>1</sup> bearing upon this same point. I have accordingly gathered a large part of Runge's material and my own in a table showing the character of the separations observed by both of us.<sup>3</sup> For the sake of clearness it may be said that Runge observed in his early observation that a triplet whose separation for my field strength would be 1.11 occurred very frequently and Runge designated this the "normal triplet." This separation corresponds to one of the four groups in barium. In yttrium, zirconium and osmium, the triplet separations would suggest that this "normal triplet" is purely arbitrary. This triplet separation gave Runge the

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value of  $1.75 \times 107$  for E/M (charge divided by mass) in the equation

$$a=\frac{\Delta\lambda}{\lambda^2}=\frac{E}{M}\left(\frac{H}{4\pi c}\right),$$

where c is the velocity of light and H the field strength.

Runge then makes the following statement: "Die bisher beobach teten pomplizierten Zerlegungen von spectrallinien in magnetischen Felde zeigen die folgende Eigentümlichkeit: Die Abstände der Komponenten von der Mitte sind Vielfache eines aliquoten Teils des normalen Abstandes 'a.' Sicher beobachtet sind bisher Teile a/2, a/3, a/4, a/5, a/6, a/7, a/11, a/12."

Under remarks in the table the abbreviations have the following meanings: N, subordinate series; S, satellite; H, principal series, *i. e.*, I. N. S. means first subordinate series satellite. The numbers refer to the special footnotes.

The most prominent feature of the table is the fact that most of the lines of the substances here studied do not belong to the types which are represented in the well-known series groups. The next prominent feature is that the types are seldom duplicated. Thirdly, great many types have common intervals, whose difference as before mentioned, consists in a variety of the factors by which the interval must be multiplied to produce the actual separation. Fourthly, whether or not the intervals are aliquot parts of a normal interval *a* is not so decisive. It can easily be contended that the intervals are irrational fractions. What is really needed is a thorough examination for a great variety of substances, to see if other lines with several components possess intervals of slightly different magnitude. Ouadruplets are scarcely serviceable for this determination as the interval cannot be determined with sufficient accuracy. Eliminating the quadruplets from the present table the intervals are not far from rational and they may be designated as aliquot parts of Runge's normal triplet a.

Fifthly, the Zeemann triplets offer no great advantages for the study of series unless the magnitudes of the separations separate into welldefined groups, as they do not in zirconium, osmium and yttrium. Furthermore, as observed in barium, the triplet groups have separations noted in lines with more components, and these are all connected by simple intervals. In substances of the zirconium class, a triplet separation becomes the more confusing, because a definite separation may be a multiple of several intervals and a separation of practically the same value, within the limits of error, be multiples of other intervals. Hence there be not more than 5 per cent. of the 410 in the group. These may be further subdivided by classification with reference to intensity. There then remains nothing to do but to try to fit an equation to the lines. Such a test means fatiguing labor as it requires three lines to determine the constants of the equation and a fourth line to test the accuracy. This method as applied to yttrium triplets was reasonably complete. In zircon only a few separations were tried. Both yielded no series.

Sixthly, series are eliminated from the lines having several components except under quadruplets of zircon designated by interval 3a/8. No series was found here.

My thanks are extended to Professor Voigt, of the University of Göttingen, at whose suggestion this investigation was undertaken.

# NOTE ON SELECTIVE REFLECTION AS A FUNCTION OF

Atomic Weight.<sup>1</sup>

BY W. W. COBLENTZ.

FTER examining the reflection and transmission spectra, one or both, of about 300 substances, the observations lying in the region of the spectrum from 0.5 to  $30 + \mu$  the writer has found that it is an easy matter to work out all sorts of relations, only to learn, after gathering more data, that the whole thing is an illusion. It therefore seems that the linear relation between the weight of the element combined with equal amounts of oxygen in the acid radical found by Mr. L. B. Morse<sup>2</sup> by selecting certain maxima of reflection bands, is misleading. From the earliest work of Abney and Feasting to the latest (theoretical) work of Einstein, it has been generally accepted that oxygen is the active element in causing certain bands, just as sulphur has been found quite inactive. The great groups of chemically related compounds have been found to have similar absorption and reflection spectra, but heretofore no simple relation could be established between the spectra of the various groups. The present simple relation results from selecting particular reflection bands from the spectra of certain carbonates, sulphates, nitrates and The selection of KNO<sub>a</sub> (max. at 7.1  $\mu$ ) from the nitrates by silicates. Morse seems arbitrary, for Pfund<sup>\*</sup> has given a large number of nitrates which have a band in common at 7.45  $\mu$ . This seems to be a characteristic band of the nitrates, and AgNO<sub>8</sub> might have been selected instead of  $KNO_{a}$ . A characteristic band of the sulphates appears to be at 9.1  $\mu$ 



9.1  $\mu$ , was selected, while Na<sub>2</sub>SiO<sub>3</sub> with a sharper band at 9.9  $\mu$ , and ZrSiO<sub>4</sub> with a group of still more intense bands, at 10.1, 10.6 and 11  $\mu$  respectively, were not considered.

In PbMoO<sub>4</sub> the maxima lie in the region of 11.75 and  $13 \mu$  while in CaWO<sub>4</sub> there is a large reflection band with maxima at about 11.4, 11.9 and 12.5  $\mu$  respectively. These data including Morse's are plotted in

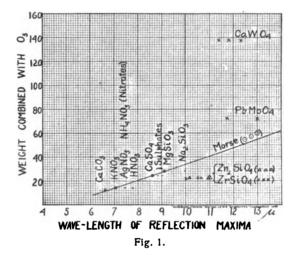


Fig. 1, and tabulated in Table I. from which it will be observed that the graph is not a straight line, and that if any relation exists it is a very complex curve, showing that for the region up to 10  $\mu$  the atomic weight

TABLE I.

Substance.	Chemical Formula.	Atomic Weight of Base.	Weight with 48 gr. of O.	Position of Band.
Calcite	CaCO <sub>3</sub>	39.7	12 gr. of C	6.6 <i>µ</i>
Potassium			-	
nitrate	KNO3	38.9	14 " " N	7.15 (7.05)
Anhydrite	CaSO	39.7	24 " " S	8.6
Enstatite	MgSiO <sub>3</sub>	24.2	28 '' '' Si	9.1
Zircon	ZrSiO,	90.6	28 '' '' Si	10, 10.6, 11 µ
Wulfenite	PbMoO4	206.9	72 '' '' Mo	11.75, 13
Scheelite	CaWO	39.7	138 '' '' W	11.4, 11.9, 12.5

of the element in the acid radical has a great effect in shifting the maximum, while beyond this point the atomic weight of the element united with oxygen is of minor importance. In fact the base and the element united with the oxygen in the acid radical seem to influence each other. As an illustration of the arbitrariness in selecting bands to establish



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relations like the aforesaid, calcite, CaCO<sub>s</sub>, may be noticed, in which the first reflection band is complex with maxima at 6.4 (?), 6.5, 6.6 and  $7 \mu$ while in its isomer, aragonite, the maxima are at 6.4 (?), 6.52, 6.74 and 7 (?)  $\mu$ . In SrCO, the band with a maximum at 6.67  $\mu$  could not be resolved even with a fluorite prism. In crystalline quartz the maxima were found at 8.4 and  $0.02 \,\mu$  while in guartz glass the reflection bands are at 7.8, 8.4 and 8.8  $\mu$  respectively. Hence, one is at a loss to know what band to select from the carbonates to compare with the sulphates, nitrates and silicates. On the other hand, in the carbonates, and in the sulphates, the maxima of the bands have been plotted in their order of occurrence, which would seem to eliminate personal bias in the selection of maxima. From this it would appear that the simple, linear relation between the atomic weight of the base and the maxima of the reflection bands in the carbonates, and in the sulphates, is in agreement, at least as a first approximation. Even with this data at hand, speculation in regard to dynamical relations among atoms in the molecules had better be postponed until more data have been procured.

The data of Morse on the reflection bands of the carbonates at 11  $\mu$  to 15 $\mu$  are of interest in connection with the question of the value of the extinction coefficient necessary to give rise to selective reflection. The transmission spectrum of a thin section of calcite shows a small absorption band at 11.4  $\mu$  which coincides with the band found by reflection. It would seem desirable to examine the transmission of thin sections of carbonates in this region of the spectrum (using polarized rays) to compare with the intensity of the bands found by reflection.

In the region of the spectrum from 10 to  $15\mu$  data can be obtained only under the greatest difficulties, and Morse's efforts have resulted in extending our knowledge throughout this region of the spectrum, verifying the previous work on the carbonates and the sulphates at  $6\mu$  to  $8\mu$ , and showing that the simple relation between the atomic weight of the base and the maxima of the reflection bands is in agreement, at least as a first approximation.

WASHINGTON, D. C., December 9, 1907.

THE USE OF COMPLEX QUANTITIES IN ALTERNATING CURRENTS.<sup>1</sup>

### BY GEORGE W. PATTERSON.

TN the year 1707 a Danish surveyor Casnar Wessal presented to the



might be represented in magnitude and direction by expressions of the form

 $r(\cos v + \sqrt{-1} \sin v)$ 

or

in which  $\epsilon$  is the base of the Napierian system of logarithms, and r and  $\epsilon^{man}$  represent the length of the line, and v and mb the angle with the horizontal; and the expressions  $\cos v + \sqrt{-1}$  sin v and  $\epsilon^{mb\sqrt{-1}}$  are the analytic representation of the direction of the line. The memoir included many other facts concerning vectors, such as addition, subtraction, multiplication, division, powers and roots, which were subsequently rediscovered by later writers, as Wessel's paper suffered the fate of being put to sleep in the little-read published proceedings of the academy.

It is evident that if v or b are variable, the line will revolve with an angular velocity proportional to the rate of change of v or b. If we indicate by j the imaginary unit  $\sqrt{-1}$ , by t the time, by  $\omega$  an angular velocity and by  $\theta$  the epoch, we may represent the instantaneous direction and sense of the revolving vector by either of the equal expressions

$$\varepsilon^{j(\omega t+\theta)} = \cos\left(\omega t+\theta\right) + j\sin\left(\omega t+\theta\right).$$

It is to be noted that  $e^{j\frac{1}{2}\pi} = j$ , and  $e^{-j\frac{1}{2}\pi} = -j$ . The analytic representation of the vector in magnitude, direction and sense is expressed by either of the equal expressions

$$r\varepsilon^{j(\omega t+\theta)} = r\left(\cos\left(\omega t+\theta\right)+i\sin\left(\omega t+\theta\right)\right).$$

The real part of such an expression, if  $\omega$ ,  $\theta$  and r are constant, may be used to represent a simple harmonic displacement, which may be defined as the projection of a uniform circular displacement upon a right line in the plane of the circle. But it is to be noted that this complex quantity as a whole represents uniform circular rather than simple harmonic displacement. In problems involving addition or subtraction the real part of the sum or the difference, respectively, will represent a simple harmonic sum or difference, and as a consequence will cause no difficulty in the interpretation of the result, for the real part of this sum or difference is the sum or difference of the real parts of the expressions to be added or subtracted; when, however, multiplication, division, powers or roots of such complex expressions are to be interpreted, an erroneous result

Memoirs of the Academy in 1799, and republished in French by the Academy, March 10, 1897. A review of this memoir is contained in Prof. W. W. Beman's vice-presidential address before section A of the American Association for the Advancement of Science at its Detroit meeting. Proc. A. A. A., 1897, Vol. XLVI., p. 33. may follow, for the real part of the result is in part due to the imaginary parts of the factors. Such an error, for example, occurs when it is desired to multiply current by E.M.F. to get power, though no such error occurs when current and impedance are multiplied together to get E.M.F. Steinmetz tries to avoid error in the product of current and E.M.F. by introducing a very artificial rule to govern such multiplication.<sup>1</sup> Other writers abandon the process and simply write the correct answer.

It then appears evident that the use of a revolving vector to represent simple harmonic quantities, while convenient because of its simplicity in cases when no error results, is on the whole hazardous. It is the object of this paper to call attention to the use in simple harmonic problems of a vector-pair, by which I mean a pair of vectors equal in magnitude and symmetrically placed with respect to the axis of reals, in other words, a pair of conjugate complex quantities. If the components revolve, they must revolve in opposite directions with equal angular velocities. The resultant of a vector-pair is always real, *i. e.*, never complex or imaginary. The vector-pair in the case of uniform circular motion of its members has as a resultant a simple harmonic quantity. This is merely stating in another form the fact that two simultaneous circular motions in opposite sense, of the same magnitude as to amplitude and frequency and in the same plane, have as a resultant a simple harmonic motion of double amplitude, but of the same frequency and lying in the same plane. This stated analytically is

$$r(\varepsilon^{j(\omega t+\theta)} + \varepsilon^{-j(\omega t+\theta)}) = 2r \cos(\omega t + \theta).$$

This result might have been deduced from the exponential formula due to Euler for the cosine, which was well known before Wessel's day,

$$\cos\,\theta=\frac{e^{j\theta}+\,e^{-j\theta}}{2}.$$

In the case of an E.M.F. following a simple harmonic law with the epoch suitably chosen, we have the following equation:

$$e = E \cos (\omega t) = \frac{E}{2} (\varepsilon^{j \omega t} + \varepsilon^{-j \omega t}), \qquad (1)$$

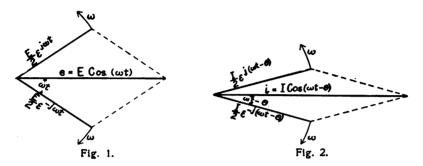
which may be represented graphically as in Fig. 1. A current following a similar law leads to a similar equation,

$$i = I \cos (\omega t - \theta) = \frac{I}{2} \left( \varepsilon^{j(\omega t - \theta)} + \varepsilon^{-j(\omega t - \theta)} \right), \qquad (2)$$

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angle  $\theta$  by which the current lags behind the E.M.F. (compare equations (1) and (2)). In both figures (1 and 2) the components of each



vector-pair revolve in opposite directions with angular velocity  $\omega$  as indicated.

The equation connecting E.M.F. with resistance, current, inductance and time,

$$e = \dot{R}i + L\frac{di}{dt} = RI\cos\left(\omega t - \theta\right) + L\omega I\cos\left(\omega t - \theta + \frac{\pi}{2}\right),$$

may be thrown into the following form :

$$e = \frac{E}{2} (\varepsilon^{j\omega t} + \varepsilon^{-j\omega t}) = \frac{RI}{2} (\varepsilon^{j(\omega t-\theta)} + \varepsilon^{-j(\omega t-\theta)}) + \frac{L\omega I}{2} (\varepsilon^{j(\omega t-\theta+\frac{1}{2}\pi)} + \varepsilon^{-j(\omega t-\theta+\frac{1}{2}\pi)}).$$
(3)

Equation (3) may be graphically expressed by Fig. 3, in which triangles, similar to the usual E.M.F. triangles rotate in opposite directions. Each triangle has its separate equation.

Remembering that  $e^{j\frac{1}{2}\pi} = j$  and  $e^{-j\frac{1}{2}\pi} = -j$ , we may represent the triangle revolving counter clockwise by

$$\frac{E}{2} \varepsilon^{j\omega t} = \frac{(R+jL\omega)I}{2} \varepsilon^{j(\omega t-\theta)}$$
(3')

and that revolving clockwise by

$$\frac{E}{2}e^{-j\omega t} = \frac{(R-jL\omega)I}{2}e^{-j(\omega t-\theta)}.$$
 (3")

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or

$$E = \sqrt{R^2 + L^2 \omega^3} I. \tag{3'''}$$

The vector-pair is of most use in power problems, for it gives correct results without introducing any arbitrary rules. No other vector method, so far as I know, gives the correct expression for the *instantaneous* value of the power, though they all by *changing the rules for multiplication* force a correct answer for its *average* value. Taking as before for E.M.F. and current

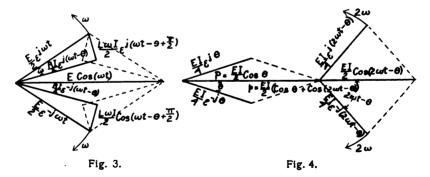
$$e = E \cos(\omega t) = \frac{E}{2} (e^{j\omega t} + e^{-j\omega t}), \qquad (1)$$

$$i = I \cos (\omega t - \theta) = \frac{I}{2} (e^{j(\omega t - \theta)} + e^{-j(\omega t - \theta)}), \qquad (2)$$

and multiplying without special rules, we obtain for the power p at any instant

$$p = \epsilon i = EI \cos(\omega t) \cos(\omega t - \theta) = \frac{EI}{4} (\epsilon^{j\theta} + \epsilon^{-j\theta} + \epsilon^{j(2\omega t - \theta)}) + \epsilon^{-j(2\omega t - \theta)} = \frac{EI}{2} (\cos\theta + \cos(2\omega t - \theta)).$$
(4)

Equation (4) brings out the important fact that power is a harmonic quantity of double the frequency of the current and E.M.F. It is, however, not simple-harmonic because the constant  $\frac{1}{2}EI\cos\theta$  is added to the simple harmonic quantity of double frequency,  $\frac{1}{2}EI\cos(2\omega t - \theta)$ . Equation (4) is graphically represented by Fig. 4, which is composed of



two vector-pairs, one stationary, and the other formed of a pair of vectors revolving in opposite senses with double angular velocity,  $2\omega$ . The constant resultant P of the stationary vector-pair represents the average value of the power as expressed in equation (5). The maximum value of the rotating vector-pair is  $P/\cos \theta$ , which is never less than P. It may equal P when the angle of lag  $\theta$  becomes zero, which is the condition for a non-

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also as

inductive circuit. The instantaneous value of the power may be expressed

$$p = P + \frac{P}{\cos\theta} \cos\left(2\omega t - \theta\right).$$

A working model to represent the various phases of the power may be made by articulating a number of rods of equal length and rotating the movable components as indicated in Fig. 4.

In case that  $\omega$  and  $\theta$  are variable quantities, Figs. 1, 2, 3 and 4 will represent E.M.F. current, E.M.F. triangles and power for more complicated harmonic (not simple harmonic) quantities, but complications of such magnitude are beyond the scope of this paper.

LABORATORY OF ELECTRICAL ENGINEERING, UNIVERSITY OF MICHIGAN, December 12, 1907.

# THE VARIATION OF APPARENT CAPACITY OF A CONDENSER WITH THE TIME OF DISCHARGE AND THE VARIATION OF CAPACITY WITH FREQUENCY IN ALTERNATING CURRENT MEASUREMENTS.<sup>1</sup>

BY BRUCE V. HILL.

### I.

SEVERAL months ago, Professor Zeleny showed that the capacity of a condenser, as measured by the ballistic method, varied greatly with the time during which the condenser was connected with the galvanometer or with the period of the instrument. In his measurements, the time of connection was estimated from the distance over which the finger of the experimenter moved at a constant rate while depressing the charge-discharge key. The first part of the present study was undertaken to gain further information on this subject. In the second part it was desired to learn how the condensers used in ordinary telephone circuits might be expected to behave toward currents of the frequency of speech vibrations, whether they would show their rated capacities (measured with currents of probably not over 60 cycles) and whether they would distort the voice currents in any way other than that calculated from the capacity and the frequency of the various harmonics of the wave.

To measure very short intervals of time, four keys were mounted in pairs on two blocks. There was a make- and a break-circuit key in each pair. Instead of using a heavy pendulum to release the keys, as is usually done, they were mounted in a vertical position, one block below the other, and near them a  $\frac{7}{8}$  inch cold drawn steel rod on which was a

<sup>1</sup>Abstract of a paper presented at the Chicago meeting of the Physical Society, December 30, 1907, to January 2, 1908. sliding weight. The friction of the weight on the rod was first carefully determined. The distances between the triggers was measured by a cathetometer. In this way  $\frac{1}{6000}$  of a second could be be read consistently. The galvanometer used was a Leeds and Northrup type P. d'Arsonval, weighted with two small bullets so that the period was 43 seconds.

Several condensers were tried : a Leeds and Northrup mica condenser, a Queen and Company's paper condenser and three telephone condensers which will be designated as A, B and C. The last was a tiny one of .25 M.F., intended for use in the base of a desk stand and had an insulation resistance so low that no measurements could be made with it. In each case the condenser was allowed to charge for a definite time and then discharged, the time between the end of the charging and the beginning of the discharge being only that required for the weight to fall a few centimeters. The time given for discharge varied from .0001 sec. to the quarter period of the galvanometer. These results are shown graphically together with the theoretical discharge curves. With the Mica condenser the apparent capacity was independent of the time of discharge. In the others the absorption is increasingly bad till, in the case of B, the discharge continued indefinitely.

### II.

Though it is known that the capacity of a condenser, measured by means of an alternating current, varies with the frequency of the current used, the exact amount of this variation seems not to be very definitely known. The method finally employed was a modification of Anderson's arrangement, in a form in which it might readily be used for rapidly determining capacities with a degree of accuracy much greater than that usually attained in commercial work of this kind.

A small inductor generator was constructed, having an ebonite disk containing sixty soft iron inductors, rotating between the poles of the field magnet, on the ends of which were wound the armature coils. Frequencies up to 3,000 could thus be obtained, this being sufficiently beyond the range of ordinary voice currents. The same condensers were used as in the first part of the experiment. The Leeds and Northrup mica condenser fell in capacity I per cent. between 60 cycles and 3,000. Condenser *B* fell 2.55 per cent. in the same range. This decrease was so small that, for the present, no attention was paid to the effect of wave

## THE

# PHYSICAL REVIEW.

# SOME STUDIES ON THE CHANGE OF ELECTRICAL RESISTANCE OF SELENIUM CELLS.

BY F. C. BROWN AND JOEL STEBBINS.

THIS paper deals with the effect of various agencies on the resistance of selenium cells. It has been found convenient to divide it into the following sections.

I. The Effect of Pressure on the Resistance.

II. The Light Sensitiveness at Different Pressures.

III. The Effect of Temperature on the Resistance.

IV. The Light Sensitiveness at Different Temperatures.

V. The Effect of Hydrogen Peroxide on the Resistance.

VI. The Effects of Radium.

VII. Discussion of Results.

VIII. Summary.

The selenium cells used in these experiments were of three kinds, those made by Ruhmer, by Giltay, and by ourselves. When exposed to light the Ruhmer cells increased in conductivity as much as twenty times, those made by Giltay as much as seventy times, and some of our own make about nine times. However we remade one of the Giltay cells and it then had a sensitiveness of 55 to I. We do not known how the Ruhmer or the Giltay cells were made. In general we used the method of making outlined by Bidwell<sup>1</sup> although we sometimes crystallized the selenium at a higher temperature than that given by him.

> <sup>1</sup> Phil. Mag., ser. V., Vol. 3, p. 351. 273

### THE EFFECT OF PRESSURE ON THE RESISTANCE.

The effect of pressure alone on the selenium cells was studied in three ways, first by liquid pressures from a Cailletet pump, second by using air pressures obtained by a Norwalk four-stage compressor, third by using liquid pressures which were maintained by air pressure. A preliminary report on the experiments made by the first method was given to the American Physical Society, February, 1904.<sup>1</sup>

In the first method kerosene was placed in the piezometer. Pressure was obtained by pumping water into the piezometer with the Cailletet pump. The water went to the bottom of the piezometer and did not affect the insulation resistance of the selenium cell.

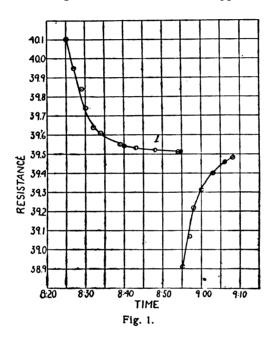
In order to get an idea of the temperature change due to compression of the kerosene a coil of no. 40 silk-covered copper wire was placed in the piezometer which was kept fairly constant in tap water at  $13.4^{\circ}$  C. The coil had a resistance of 39.51 ohms at  $13.4^{\circ}$  C. After the resistance of the coil had become constant it was assumed that the temperature of the kerosene was the same as that of the tap water. Then the pressure was raised to 425

kgm cm <sup>3</sup>	Ohms Resistance.	. Time.	Temperature.
1	39.51	8 : 20	13.4° C.
425	40.11	8:25	
420	39.95	8:27	
420	39.84	8:29	
420	39.74	8:30	
420	39.64	8:32	
420	39.61	8:34	
420	39.55	8:39	
420	39.54	8:40	
420	39.53	8:43	
420	39.52	8:48	
420	39.51	8 : 54	
420	39.51	8 : 54 <u>1</u>	
1	38.91	8:55	
1	39.06	8 : 57	
1	39.21	8 : 58	
1	39.31	9:00	
1	39.40	9:03	
1	39.46	9:06	
1	39.48	9:08	

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kgm./cm<sup>3</sup>. and maintained at 420 kgm./cm<sup>3</sup>. until the coil had returned to the resistance that it had previously at atmospheric pressure. Then the pressure was suddenly lowered to atmospheric pressure and the kerosene was thereby cooled the same amount it had been heated previously by the compression. The resistance was measured at the intervals shown in the table above.

These observations show conclusively as is readily seen from Fig. 1, that the change of resistance in the copper coil is mainly



if not entirely due to temperature change. For when the kerosene is compressed and heated it returns to the temperature of the tap water and at about the same rate as that when the kerosene is cooled by letting the pressure off. We see that in thirty minutes the kerosene has returned to the temperature of the tap water when the pressure was suddenly raised or lowered 420 kgm./cm<sup>2</sup>. It is to be noted that the resistance changed the same amount and oppositely when the pressure was lowered as when it was raised. Roughly one ohm change of resistance signifies seven degrees change of temperature. After 20 minutes the coil had returned within .2 degree and in 10 minutes it had returned to within one degree. This was when the change of pressure was 420 kgm./cm<sup>2</sup>. and when the coil was in a hard rubber case. If the pressure change were less the temperature change would be correspondingly less.

In all cases some modification of the Wheatstone's bridge method was employed to measure the resistance.

The following are some of the first observations with selenium cells under pressure. One of our own cells no. 4a was used. The piezometer was kept in tap water at 14.8 to 16.° C.

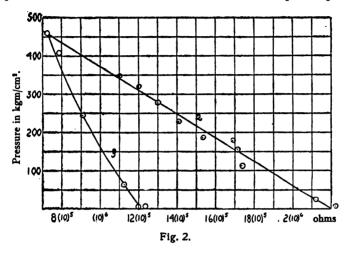
E.M.F. in Circuit Volts.	Pressure, kgm/cm <sup>3</sup> .	Resistance, Ohms.
1.4	450	650,000
	270	1,300,000
	350	1,100,000
	320	1,200,000 after 10 minutes
	. 220	1,440,000 '' 40 ''
	185	1,530,000
	180	1,700,000
	160	1,720;000
	80	1,730,000
	20	1,920,000
	22	1,940,000
	1	1,990,000 after 10 minutes
10.0	1	1,170,000
	240	900,000
	400	770,000
	495	720,000
	450	770,000
	70	1,120,000
	72	1,100,000
	1	1,230,000
	1	1,200,000 after 10 minutes

These data are shown in curves 2 and 3 (Fig. 2). When 1.4 volts are used in the circuit, the average change of resistance per atmosphere is 2,200 ohms. When 10 volts are used the change of resistance is about 1,100 ohms per atmosphere. In the first case the percentage change is .11. In the second case it is .05.

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data are shown graphically in Fig. 3. The mean percentage change per atmosphere is .12.

Similiar results were obtained with other cells. One cell no. 6 with platinum electrodes had a resistance at atmospheric pressure

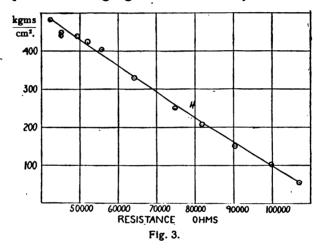


of 1,670,000 ohms. Its average decrease per atmosphere was .11 per cent. To compare these three cells, one having round copper electrodes, one with flat copper electrodes and one with platinum

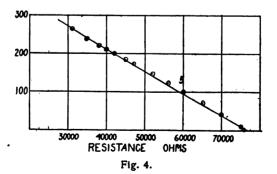
Time.	Pressure, kgm/cm <sup>2</sup> .	Resistance, Ohms.	Change of Resistance per Atmosphere.
2:52 P. M.	490	44,600	144
2:54	496	44,600	
2:57	570		
2:59	490	42,400	147
3:15	490	48,700	
3:20	478	49,700	
3:38	453	51,700	139
3:45	440	53,100	140
4:15	405	56,000	
4:25	333	64,300	
4:30	250	74,600	156
4:35	208	81,900	160
4 : 39	150	90,500	
4 : 44	102	99,900	138
4 : 47	59	106,900	
5 : 18	1	{ 115,000 { 112,000	

electrodes, when 1.4 volts were used in the circuit, the change of resistance was .11 per cent., .12 per cent. and .11 per cent. respectively.

The conductivity of these cells was about doubled when they were exposed to strong light. However they were made at dif-



ferent times and had electrodes of different shape and material, and the initial resistance is seen to vary more than ten times. It would seem that for selenium cells of a given light sensibility and with con-



In studying air pressures the selenium cells were placed is a piezometer made of car axle steel. The piezometer was connected in series with a steel tank of about 15 cubic feet capacity. The tank was so fitted with valves that the pressure could be let off the piezometer without lowering the pressure in this supply tank. The pressure was furnished by a Norwalk four-stage compressor. About a month before this work was begun with selenium the compressor and tank were used in connection with the liquid-air plant. Lime and potassium hydrate were used as purifiers in the plant. In the first few experiments the air used for pressure was drawn through lime.

Giltay cell no. 92 was the first to be studied in air pressure. On May 20, at atmospheric pressure and about  $23^{\circ}$  C., the resistance was 1,300,000 ohms in the dark. When 1,400 pounds pressure was applied, the resistance first fell to about 1,200,000, but it kept on decreasing and after about two hours it had reached 520,000 ohms with the pressure on. When the pressure was taken off the resistance recovered immediately to 590,000 ohms.

The condition of the cell afterwards was as follows :

May 22,	1,100,000 to 1,000,000 ohms.
May 23,	14,300 ohms after being under 400 pounds pressure 12 hours.
May 23,	14,400 ohms at atmospheric pressure.
May 24,	7,100 ohms.
May 27,	10,500 ohms.
July 15,	10,300 ohms.

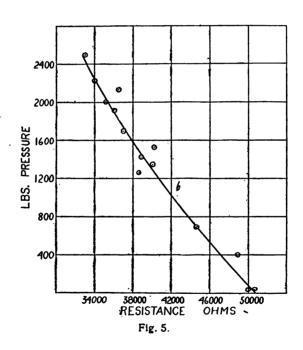
On the last date the selenium was remelted and recrystallized. Its resistance was as follows :

10,300	ohms at	27	°C.	
6,000	**	150	"	
1,700	**	204	"	
770	"	209	"	
770	"	213	"	
20,000		150	"	
80	"	219	"	
~	44	218	"	selenium melted.
6,400	**	155	"	
1,900	**	200	"	
4,000	"	183	"	
2,700,000	44	25	"	
50,000	**	25	**	10 cm. from 16 c.p. light.
2,600,000	64	25	**	in dark again.

It is evident from the above table that the resistance of the cell decreased still further as the temperature was raised.

We then tried four cells of our own make under air pressure, and every one behaved just as the Giltay cell did. After being under air pressure from one to twenty hours the resistance reached a final value from which the cells did not recover.

Next the piezometer was filled with kerosene and the pressure was maintained by the air pressure bearing on the surface of the liquid. Several cells were tried and there was no permanent break-



ing down of the resistance in any case. When the pressure was raised or lowered the cell changed its resistance almost instantly.

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percentage decrease of resistance per atmosphere is seen to be about .22.

We are not prepared to say why the first cells broke down in resistance under air pressure and the last ones did not. There may have been something in the pressure system which was blown out before the last set of observations were taken. The benzene or oil may have prevented the action of the air in the cases in which the resistance did not break down. We do not think the structure of the cells was different in the two cases.

THE LIGHT SENSITIVENESS AT DIFFERENT PRESSURES.

The selenium cell used in these experiments was the Giltay no. 92 after it had been remelted and reannealed. It was fixed in a hard rubber mounting so that it could be easily and rigidly fastened to electrical connections entering from the side of the piezometer.

The piezometer was made from car axle steel. It was provided with electrical connections similar to some described by Knipp.<sup>1</sup> Opposite one of the electrical connections was an opening to the pressure tank. Opposite the other was a plate-glass window to allow the entrance of light to the cell.

After having considerable difficulty with air pressure around the cell it was decided to use liquid pressure. The piezometer was nearly filled with kerosene, which not only protected the cell from breaking down but also diminished the errors due to temperature. The fact that it absorbed considerable light did not lessen the accuracy of the results.

At first the cell was illuminated by an amyl-acetate standard candle but it was difficult to keep the candle adjusted. The results here published were obtained when an incandescent light giving about I c.p. was placed at a distance of 15 cm. from the cell. The time of exposure was 10 seconds. It was regulated by a knife switch placed in the circuit. The light was run by a storage battery giving 6.21 volts during the experiments.

The change of resistance was measured by placing the cell in one arm of a Wheatstone's bridge. A Leeds and Northrup Type H, aperiodic galvanometer was used. The deflection given when the cell was illuminated was taken as indicative of the change of

<sup>1</sup> PHYS. REV., X1., 129.

resistance. This change was found directly by finding what known change of resistance would produce the same deflection. The period of the galvanometer, 3 seconds, and the time of exposure, 10 seconds, were such that no appreciable error entered in the final results. Longer exposures would have been used had it not been that the time for recovery of the light sensitiveness would have increased. Before beginning a series of observations the cell was exposed to the incandescent light for a minute. Then after threeminute intervals the cell was exposed for 10 seconds and the readings were taken. Using constant time intervals insured the same stage of recovery. The same error entered with the pressure on as with the pressure off.

The sensitiveness was compared at pressures varying from 15 pounds to 2,500 pounds. Following is a sample of the series of readings taken. The electromotive force in the Wheatstone's bridge circuit was 11.9 volts.

Time.	Resistance of Selenium Cell.	Read	lings.	Deflection in mm.	Ohms Change of Resistance.	Percentage Change.	Pressure, Lbs.
3 : 21		- 3.0	27.0	30.0			
3:24		15.6	44.6	29.0			
3 : 27		23.4	52.4	<b>29</b> .0			
	2,400,000			29.3	225,000	9.38	15
3 : 30		- 19.7	13.5	33.2			
3 : 33		- 35.3	- 1.5	33.8			
3 : 36		<b> 39</b> .8	- 6.0	33.8			
	1,860,000			33.6	159,000	8.55	1 <b>,970</b>
3 : <b>39</b>	1	- 20.0	8.7	28.7			
3 : 42		0.8	29.7	28.9			
3 : 45	, i }	12.0	40.8	28.8			
	2,520,000	1		28.8	241,000	9.56	15
3 : 48		- 13.5	18.0	31.5			
3 : 51		- 36.6	- 4.0	32.6			
3 : 54		- 45.6	- 13.3	32.3			
	1,970,000			32.1	170,000	8.63	1, <b>890</b>
3 : 58		- 33.4	- 4.3	29.1			
4 : 01		- 12.4	16.5	28.9			
4:04		- 0.3	28.2	28.5			
	2,660,000			28.8	270,000	10.15	15

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Series.	<u> </u>	II.	111.	IV.
Mean resistance of selenium ( pressure on	2,607,000	2,270,000	2,133,000	1,915,000
cell, ohms. (pressure off	2,850,000	2,878,000	2,435,000	2,530,000
Mean pressure, lbs.	730	2,075	525	1,930
Change of resistance due to pressure on light action.	185,000 220,000	131,000 <sup>°</sup> 200,000	149,000 178,000	164,000 245,000
Percentage change of resist- { pressure on ance due to light. { pressure off	7.11	5.77 6.92	6.99 7.32	8.59 9.70
Change of light effect due to pressure.	0.59	1.15	0.33	1.11
Change of light effect per lb. pressure.	.00083	.00056	.00065	.00058

SUMMARY OF RESULTS ON LIGHT SENSITIVENESS AT VARIOUS PRESSURES.

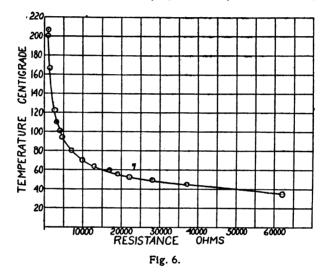
Area of cell exposed, from .3 to .4 sq. cm.

From the preceding data we get a small but measurable variation in the light sensitiveness at different pressures. For the percentage change of resistance per pound of pressure, the lowest value is .00056 and the highest is .00083. This variation in the different series may have been produced by different temperatures, or by having different areas exposed to the light. However the variation in the candle power of the light may be considered zero. Also the error due to time of exposure was practically zero.

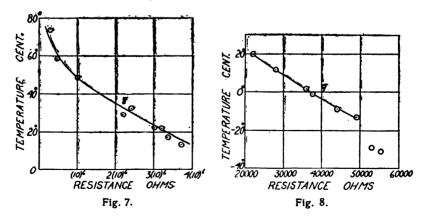
Probably the greatest source of error was due to temperature variation. When the air pressure was turned on from the large supply tank, there was some heating effect in the cell due to the compression of the kerosene. The air in contact with the kerosene probably did not have any immediate effect on the temperature of the cell. In order to approximate the temperature change when the air was turned on, a copper coil was placed in the piezometer. Its resistance was 44.05 ohms at 27.5° C. at atmospheric pressure. One minute after 1,500 lbs. pressure was applied the resistance was 44.20 ohms. After two minutes 44.07 ohms and four minutes 44.06. In five minutes then the temperature had practically returned to its original value.

During the experiments the temperature of the piezometer varied between 24° and 27.5° C., and it was estimated that the cell did not vary more than this. The variation from 6.92 to 9.70 per cent. in the different series may have been partly due to temperature. It was more probably caused by slight differences in the adjustment of the selenium cell and its position with respect to the light. THE EFFECT OF TEMPERATURE ON THE RESISTANCE.

The effect of temperature on the resistance of the selenium cell is shown in curves 7, 8 and 9 (Figs. 6, 7, 8), for the temperatures



indicated. Two points are to be noted, the amount of variation with temperature and the similarity of the variation in the three cells. If the percentage change of resistance were plotted against temper-



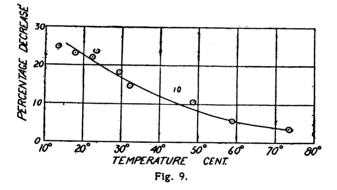
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Evidently it would be more satisfactory if we could determine the effects on selenium in terms of specific resistance, but this cannot be done accurately because of the variable amount of selenium in a cell and the structure of the cell.

LIGHT SENSITIVENESS AT DIFFERENT TEMPERATURES.

To determine the sensitiveness at different temperatures, the Giltay no. 92 was connected in one arm of the Wheatstone's bridge. The cell was placed in a kerosene bath surrounded by a water-bath. About I sq. cm. area of the cell was exposed to an incandescent light, of about I c.p., and at a distance of 15 cm. About one fifteenth of the total area of the cell was illuminated. The cell was illuminated by light passing above the surface of the water-bath. The thickness of kerosene passed through was not much different from that passed through by the light in the pressure-light experi-



ments. The current for the light was obtained from 3 storage batteries giving 6.21 volts. The time of exposure (10 seconds) was regulated by a knife switch. When the cell was exposed there was a deflection of the galvanometer in the manner explained in a previous section and the change of resistance was calculated.

The temperature of the cell was regulated by the surrounding water-bath, which was heated with a bunsen burner or cooled with ice shavings. It will be noticed from the following data that these results are taken as nearly as possible under the conditions prevailing in the study of light sensitiveness at different pressures. These data are shown graphically in curves 10 and 11 (Figs. 9, 10). In curve 11 we have the sensitiveness expressed for different values of the resistance of the cell, this resistance being a function of the temperature. This resistance is also a function of the state of recovery of the cell and other conditions. But the sensitiveness is probably a function of all these conditions. Consequently

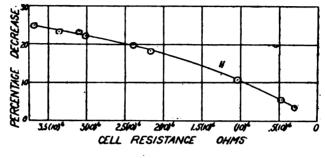


Fig. 10.

we should expect more concordant results in curve 11, since the experiments were made on different days when the state of recovery was different.

THE EFFECT OF HYDROGEN PEROXIDE ON THE RESISTANCE.

We wish to give here some of our own meager observations on the effect of hydrogen peroxide in order to make comparisons with other phenomena.

A cell having a resistance of 80,000 ohms decreased to 50,000 ohms when placed 5 cm. above a surface of hydrogen peroxide. But when the surface of the hydrogen peroxide was enveloped by a sheet of lead, copper, aluminium or even paper there was no appreciable change in the resistance from 80,000 ohms. However, if any of these sheets did not completely cover the surface of the liquid, merely shutting off all the straight line paths from the surface of the hydrogen peroxide to the selenium cell, then the change of resistance was almost as marked as in the first case. When a cell decreased in resistance owing to neighboring hydrogen peroxide, its recovery seemed to be slower than recovery from light,



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` Time.	Tempera- ture, Cen- tigrade.	Resistance of Cell in Ohms.	1 	Readin	igs.	Defiec- tion, mm.	Change of Resist- ance.	Percen- tage Change of Resistance
1:54 P. M			-	1.8	62.5	64.3		
1:57			-	4.0	60.3	64.3		
1:60			-	4.0	59.8	63.8		
2:03			-	4.2	59.3	63.5		
	22.3°	3,045,000	1			64.0	670,000	22.0
2:39				8.0	69.2	61.2		
2:42			İ	0.4	62.5	62.1		
2:45			-	0.2	62.0	62.2		
2:48			-	0.2	62.1	62.3		
	17.9	3,370,000				62.0	780,000	23.1
3 : 25				2.0	63.4	61.4		
3:28			-	0.8	61.0	61.8		
3:31			-	0.8	60.4	61.2		
3 : 34			-	0.8	60.4	61.2		
	13.2	3,725,000				61.4	927,000	24.9
4 : 15			-	5.9	63.5	69.4	-	
4:18		•	-	10.0	59.9	69.9		
4:21			-	13.0	56.6	69.6		
4:24			-	15.7	53.0	68.7		
	29.1	2,180,000				69.4	397,000	18.2
5:00			-	47.5	28.0	75.5		
5:03			- :	109.0	33.0	76.0		
5:06			-:	169.6	92.5	77.1		
5:09			-:	231.5	154.0	77.5		
	58.6	487,000				76.5	27,400	5.6
9:06 A. M.			-	14.2	50.4	64.6		
9:09			-	16.3	48.5	64.8		
9:12			-	18.4	46.0	64.4		
9:15			-	19.2	44.0	63.2		
	23.1	3,212,000				64.2	750,000	23.3
LO : 42				9.0	86.3	77.3		
LO : 45				14.0	85.0	71.0		
LO:48			-	5.3	74.6	79.9		
10 : 51			-	4.0	72.0	76.0		
	73.4	284,000			1	76.0	10,400	3.7
2:00			-	3.5	69.2	72.7		
2:03			-	30.2	43.3	73.6		
2:06			-	51.6	21.6	73.2		

LIGHT SENSITIVENESS AT DIFFERENT TEMPERATURES.

Time.	Tempera- ture, Cen- tigrade.	Resistance of Cell in Ohms.	Readi	ngs.	Defiec- tion, mm.	Change of Resist- ance.	Percen- tage Change of Resistance	
2 : 19 P. M.			- 7.0	62.7	69.7			
2:22			- 11.2	58.7	69.9			
2:25			- 14.7	53.6	68.3			
2:28			- 18.2	51.3	69.5			
	32.2	2,410,000			69.4	479,000	19.9	

LIGHT SENSITIVENESS AT DIFFERENT TEMPERATURES. - Continued.

pressure or radium effects. It seems that the decrease of resistance was due to something diffusing from the hydrogen peroxide. Certainly there was no radiation of the slightest penetrating power.

In order to study the nature of this change in the selenium cell, we superimposed a light effect upon the hydrogen peroxide effect.

Hydrogen peroxide of strength 30 per cent. was poured on black paper and black cloth within 4 cm. of the Giltay cell no. 92. Some hydrogen peroxide may have got on to the cell itself. The resistance fell from 2,200,000 ohms to 10,000 ohms. Apparently it did not begin to recover until the hydrogen peroxide had evaporated. The time taken was about 20 minutes. When illuminated at this low resistance by a I c.p. light, at 30 cm. distance, there was no appreciable change in the resistance. There was no light effect at 18,000 ohms, but when the cell had recovered to 50,000 ohms, a deflection of 5 mm. was produced on the scale, when the cell was illuminated for 10 seconds. The value of the change in resistance was not measured, but it was very small. These results seem to show in a rough way that where there is already a maximum effect due to hydrogen peroxide, there will be produced no additional effect by superimposing a light effect. Also that the light effect will be correspondingly less as the hydrogen peroxide effect increases.

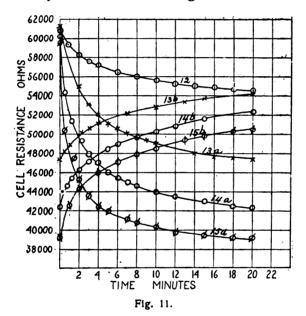
#### THE EFFECT OF RADIUM.

Under this head is given : (1) The resistance of the selenium cell

The radium used in these experiments was 3 mgm. of 2 to 3,000,000 activity, kindly lent by Professor Rutherford. It was in a rubber case with a mica cover. The mica cover could be removed.

The selenium cell used was made by Ruhmer and numbered by him 454. Its conductivity was increased about 8 times when exposed to light. The circular area exposed to radium was 2.3 cm. diameter.

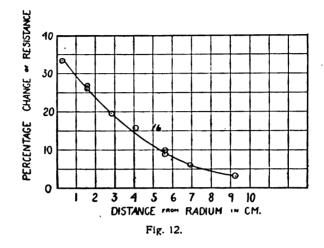
The resistance was measured by the ordinary Wheatstone's bridge method. The cell was fixed in a hard rubber case. This case was lowered till it touched the top of a brass cylinder 2 inches in diameter. Cylinders of different lengths were used so that the



effect at different distances could be obtained without disturbing the radium or exposing the cell to light. The results with radium and selenium are shown in the curves of Fig. 11.

Curve 12 shows the decrease of resistance with time when the perpendicular distance from the radium to the cell is 2.6 inches. Curve 13*a* shows the same when the distance is 1.1 inches. Curve 14*a* shows the effect when the distance of the radium is .6 inch, and curve 15a is for a perpendicular distance of .1 inch. The general results of the above-mentioned curves and other similar ones are shown in curve 16 (Fig. 10) in which the exposure is taken for 10 minutes.

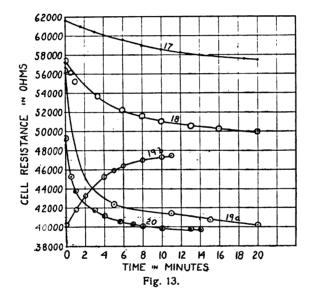
The number of particles or rays striking the surface of the sele-



nium should vary as the solid angle, if there were no absorption in the intervening space. The following table shows how the change of resistance varies with the solid angle.

		_ =					
Distance of the Radium, mm.	2.6	15.3	27.9	40.6	66	78.7	102.5
Solid angle. Percentage change of resistance.	1.5 π	0.4 π	0.15 π	<b>0.078</b> π	0.03 π	<b>0.022</b> π	$0.012 \pi$
Percentage change of resistance.	33.0	26.5	18.5	16.0	9.5	6.2	3.0
					<u> </u>		

From these data it is seen that the change of resistance does not vary as the solid angle. The absorption of the particles by the air does not appear to be capable of explaining the discrepancy. We know that for intense lights the change of resistance is not proportional to the intensity of the light. In the same way we might expect for large values of the solid angle that the change of resistance would not be proportional to the number of particles falling on the selenium surface. Further discussion of the foregoing results will be postponed until the effect of placing thin sheets of mica between the radium and the selenium cell has been considered. The curves of Fig. 13 show the decrease of resistance of the cell with time when the cell is 1.3 cm. away from the radium. The curves show how the effect varies with time with different thicknesses of mica between the cell and the radium. Of course there was 1.3 cm. of air between the cell and the radium in every case. In obtaining the data for curve 18 the radium was covered with a mica sheet .017 cm. thick. For curve 17 there was an additional mica sheet



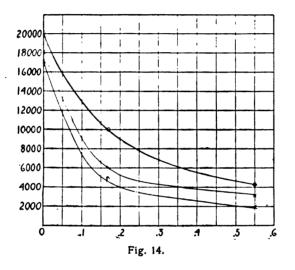
.038 cm. thick making a total thickness of .055 cm. But for curves 19a and 20 there was no mica over the radium. The difference in these two curves arises from the fact that the state of recovery was not the same in the two cases. Only 14 minutes was allowed for recovery after getting the data for curve 19a before taking the observations represented by curve 20.

Fig. 14 shows approximately how the effect varies with different thicknesses of mica interposed. The data for these curves were taken from curves 17, 18 and 19*a*. It could only be approximated however because the state of recovery was different hand the thinnest piece of mica used would not permit any of the a particles to penetrate it. It therefore follows that some part of the effect is due to the  $\beta$  particles.

The intensity of the  $\beta$  particles after passing through an absorbing medium is expressed by the equation,

$$i=i_0e^{-\lambda d},$$

where  $i_0$  is the value of the intensity for no absorbtion, d is the thickness of the absorbing material, and  $\lambda$  is the coefficient of absorption.



To find the coefficient of absorption from our data we may take from curve 23 the intensity of the radiation after passing through .02 and .05 cm. of mica. For either of these thicknesses the intensity of the radiation is about proportional to the change of resistance, and also there can be no  $\alpha$  particles in either case. From the previous equation we get for different thicknesses of mica,

$$\lambda = \frac{\log_e \frac{i_1}{i_2}}{-d_1 d_2}$$

Putting in the values for a 5 minute exposure we get

$$\lambda = 23.0.$$



For a 10-minute exposure as taken from curve 22, the value of the coefficient is

$$\lambda = 14.2.$$

Strutt gives 10.8 for the value of  $\lambda$ , the coefficient of absorption, for the  $\beta$  rays from radium. Our values are of the same order of magnitude as that given by Strutt.

In order to see if the  $\alpha$  particles play any part in the change of resistance, we may refer again to curve 23. If we assume the density law for the absorption of the  $\alpha$  particles, they would be almost completely absorbed by .015 cm. of mica. Assume then that all the change of resistance, 5,200 ohms, when .015 cm. of mica is interposed is due to the  $\beta$  rays. By use of the equation  $\log i/i_0 = e^{-\lambda d}$ it is found that if 5,200 represents the intensity of the  $\beta$  rays after passing through a thickness of mica of .015 cm., then the intensity for no absorption should be represented by 7,400. For these intensities the change of resistance should vary less rapidly than the change of intensity, so that for zero thickness of mica, we should expect a change in resistance of less than 7,400 ohms. But the curve 23 shows that the change of resistance for no mica interposed is 17,000 Since this value represents a larger value of the intensity, ohms. we are led to believe that where there is no absorption the  $\alpha$  particles have a greater effect than do the  $\beta$  particles. However we do not know whether any of this effect which we have attributed to the  $\alpha$  particles may be due to the emanation.

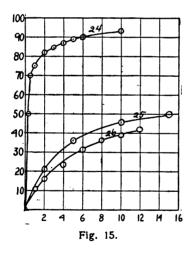
Again referring to the variation of resistance with distance from the radium it is seen that beyond 5 cm. the change of resistance is almost proportional to the solid angle subtended. The slight discrepancy here can be accounted for by the absorption of the  $\beta$  particles in air. The  $\gamma$  particles would suffer no appreciable absorption under such circumstances. For distances less than 5 cm. the change of resistance decreases less rapidly than does the solid angle. But no conclusions can be drawn from this since the change of resistance is not proportional to the intensity.

The effect of radium on the selenium cell has been investigated by Himstedt and Bloch. Himstedt<sup>1</sup> found a one per cent. decrease of resistance in the selenium cell. The radium rays had to pass

<sup>1</sup> Ann. der Physik, 1901, 4, p. 535.

through an opaque paper and one centimeter of air. Bloch <sup>1</sup> found a cell to decrease from 30,100 to 29,000 ohms and this through a sheet of paper. In another case a cell decreased from 654,000 to 640,000 ohms in 10 minutes time. The radium used was of activity about 1,000. Himstedt does not state the activity of his radium, but judging from the percentage decrease it was probably not much different from that used by Bloch. In either of these cases the effect was so slight and the data so limited that we could not expect to arrive at any conclusion as to how the radium affected the selenium.

The recovery of the selenium cell after exposure to radium is shown in curves 13b, 14b, 15b, 19b and 26. It is apparent that the



recovery is not as rapid as the recovery from the same decrease of resistance due to light. However it does return eventually to approximately the initial value. In curve 26 (Fig. 15) is shown the recovery when there was about a 35 per cent. decrease of resistance due to radium. Curve 25 shows the recovery when the same Ruhmer cell had its resistance decreased 87 per cent. by light. Unfortunately the recovery for a 35 per cent. decrease was not studied, but the recovery would evidently be

much faster. In curve 25 is shown the recovery of cell 4 when there was a 10 per cent. decrease of resistance by light. The conclusion is that for the same decrease of resistance the recovery from the effect of radium is much slower than the recovery from the effect of light.

DISCUSSION OF RESULTS.

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relate them in so far as possible. The selenium cell varies in resistance when exposed to temperature change, to pressure change, to light, to radium rays, to hydrogen peroxide and to other conditions not mentioned in this paper. The question arises as to whether these resistance changes are ultimately due to the same cause. We may state at the outset that we cannot completely correlate our results but we hope that in the near future an hypothesis may be set up which will satisfactorily and completely explain all the various selenium phenomena.

First as regards pressure. The pressure effect must be a genuine effect in the selenium. The change in resistance due to pressure cannot be due to change in contact resistance between the selenium and the electrodes. For suppose,

R is the contact resistance.

r is the variable resistance in the selenium itself.

 $\Delta R$  is the change of contact resistance due to pressure.

 $\Delta r$  is the change of resistance due to light.

Then when the pressure is off, the percentage change of resistance in the whole cell would be

$$\frac{\Delta r}{R+r} \times 100.$$

When the pressure is on the cell, the light effect being the same, the percentage change of resistance would be

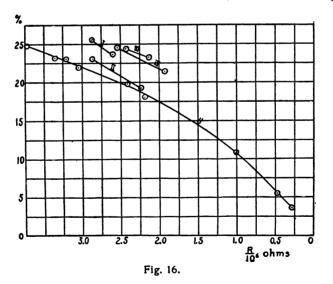
$$\frac{\Delta r}{R+\Delta R+r} \times 100.$$

The ratio of the percentages of change would be,

$$\frac{\text{pressure on}}{\text{pressure off}} = \frac{R+r}{R+dR+r}.$$

If the pressure decreased the contact resistance,  $\Delta R$  would be negative, and the ratio necessarily greater than one. On examining our data it is seen that the value of this ratio is slightly less than unity in every case, and it is clear then that the change of resistance due to pressure cannot be due to change of contact resistance. We may also arrive at the same result by other reasoning.  $\Delta R/R$  is considerable, sometimes approaching values as large as .5. If the change due to pressure were in the contact between the selenium and the electrodes, we should expect a variation in the light sensitiveness approaching values as large as 50 per cent. But in comparison with values as large as 50 per cent. the variation may be considered zero.

Next consider the similarity of the nature of the decrease of resistance due to temperature and that due to pressure. It is to be noted that in pressure effects as well as in temperature effects the sensitiveness of the cell to light seems to be a function of the resistance of the given cell. This can best be understood by looking at the curves of Fig. 16. In I., II., III. and IV. is shown how the sensitiveness varies with the resistance, when the change of



resistance is produced by a variation of the pressure. In series IV. of the observations on the sensitiveness at different pressures it was estimated that a square of the cell was exposed to light

#### No. 4.] ELECTRICAL RESISTANCE OF SELENIUM CELLS. 297

Within the limits of error of the experiments it is seen that the rate of change of sensitiveness is the same for all the curves, and we may conclude that the sensitiveness to light is probably dependent upon the resistance, whether that be conditioned by temperature or pressure.

It is seen from the previous data that the pressure effects take place almost instantly upon the application of the pressure. With the exception of a small lag the selenium cell, when exposed to temperature changes in a liquid bath, rises to a position of electrical equilibrium even quicker than does an ordinary thermometer. This correlation is what we should expect. However if the quantity of selenium in the cell is great and the cell is surrounded by an air bath, the cell may be quite sluggish in changing its resistance with the temperature of the bath.

The rough work done with hydrogen peroxide will not of itself permit of any definite conclusions, but the following seems to be true. The change of resistance in the dark is of such a nature that if light is allowed to fall on the cell there is no additional change in the resistance, providing only that the change produced by the hydrogen peroxide is sufficiently great. The rate of recovery from exposure to hydrogen peroxide is very slow, resembling the recovery from the effects of radium.

With increased temperature or increased pressure, or hydrogen peroxide exposure the change of resistance due to light is correspondingly less. So far as electrical conductivity is concerned, all these conditions seem to take the selenium toward a certain equilibrium state.

#### SUMMARY.

1. The selenium cell changes its resistance with a change in the mechanical pressure on its surface. The pressure produces a real change in the resistance of the selenium itself. For the cases noted the percentage change of resistance for one atmosphere lies between .05 and .30. This value is also a function of the temperature and the electromotive force applied in measuring the resistance.

2. An increase of pressure or a rise of temperature lowers the light sensitiveness of the selenium cell.

3. The light sensitiveness is a function of the resistance of the given cell, whether this resistance be conditioned mainly by temperature, light, radium or hydrogen peroxide.

4. The effect of radium and of hydrogen peroxide is to decrease the resistance very markedly, as much as 35 and 99 per cent. respectively.

This work was carried on in the Physics laboratory of the University of Illinois and the writers wish to acknowledge their indebtedness, to Professor A. P. Carman for apparatus placed at their disposal and for his help in the early part of the work; also to Professor E. Rutherford for kindly lending the radium used, and to Professor O. W. Richardson for several valuable suggestions.

UNIVERSITY OF ILLINOIS, PRINCETON UNIVERSITY, November 1, 1907.

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# PENDULUM COINCIDENCES DETERMINED BY SHADOW REENFORCEMENTS, SHADOW MICROMETRY, ETC.

#### By C. BARUS.

I. Let two similar pendulums be mounted, one normally behind the other relatively to their nearly parallel planes of vibration. Provide each (light cork attachment and incision) with a small square of wire gauze (one inch square) of about a millimeter mesh, the planes of the gauze being nearly normally behind each other, about six inches apart, and parallel to the plane of vibration. Let the threads of the gauze be respectively horizontal and vertical (or in general nearly parallel in the two cases) and let the pendulums be swung over about the same arc.

2. When the pendulums are at rest, the observer looking from a distance through one gauze at the other with a bright background behind it (white paper, spot of sunlight, ground glass and lamp), sees the usual shadow reënforcements, in form of more or less equidistant horizontal and vertical dark bands. When the pendulums move the vertical bands are usually wiped out except at the elongations, because the corresponding wires of the gauze sweep past each other too rapidly to be recorded by the eye. The horizontal bands, however, remain in the field, for there is no translation in the direction of the axis of a pendulum; but there is rotation. Hence, as the pendulums sweep over any angle  $\alpha$  with respect to each other, the originally horizontal shadow bands sweep over a large multiple of  $\alpha$ . Thus the shadow bands are seen to topple from an angle of more than  $\Delta f_{1}$  degrees

and  $\gamma$  the angle of the shadow bands with the direction of either of the wires; if *a* is the distance apart of the wires and *b* the projection of the *a* of one on the plane of the other by the eye of the observer, so that *a* and *b* are the virtual distances apart of the effective wires, we may write  $\tan \gamma = a \tan a/(a - b \sec a)$ , and thus  $\gamma$  is liable to be greater than 90 degrees. If *a* is small  $\tan \gamma = aa/[(a - b) - aa^2/2]$  and for very small *a*,  $\tan \gamma = aa/(a - b)$ . Since *a* and *b* are nearly equal the rapid increase of  $\tan \gamma$  as *a* passes through zero is manifest.

3. The phenomenon is very beautiful. With a larger square of wire gauze (6 inches square and  $\frac{1}{8}$ -inch mesh) it may be easily shown to a class on a light background. When the two pendulums are all but stationary, the horizontal bands are also nearly so, while the vertical bands are now permanently in the field magnifying the motion and becoming fixed at the coincidences. Pendulums may be thus compared which are scarcely seen to move, though for this purpose the method of the next paragraph is still better. Finally the phenomenon may be projected in various ways, but in no case are the results so satisfactory as the above. If two pendulums vibrate at right angles to each other, the elongations of the vertical pendulum are useful in the same way, horizontal bands recurring and marking the coincidences of the upper elongation of the vertical pendulum and the mean position of the horizontal pendulum.

4. The most fascinating reinforcements are obtainable from the superposition of two identical sets of concentric circles, which may be drawn or photographed on glass plates. If the circles are equidistant the hyperbolæ of Young's interferences are strikingly brought out for all distances apart of the centers. If these shadow bands are to be straight lines, equidistant and at right angles to the lines ioning the centers of the two plates, the *n*th and (n + 1)th

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To use this arrangement as a micrometer, suppose the distances to be measured by the relative motion of the two superposed plates are in a horizontal direction, and let x be one of these small distances. Let the plates be placed in a vertical plane through x, and so that the center, c, of one set of circles may be a centimeters above the center, c', of the other set of circles. Then if  $\gamma$  is the angle of the dark bands (normal to cc') with the horizontal x,  $\tan \gamma = x/a$ . Thus if a is one tenth millimeter, a displacement of x will rotate the originally horizontal bands (cc' vertical), rising or falling according to the relative motion, roughly about as follows:

x = .002 .005 .01 .03 .1 millimeter  $\pm \gamma = 1^{\circ}$  3° 6° 17° 45°

The distance apart of the bands is uniformly  $1/2\sqrt{x^2 + a^2}$  or  $1/2(x^2 + a^2)$  of the distance apart of centers; and they thus become wider as x and a decrease, vanishing at infinity in case of coincidence. Finally if a medium could be constructed in which the index of refraction increases about as the normal distance from the lines joining the centers, the present phenomenon would approximately replace Young's interferences.

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# A SATISFACTORY FORM OF HIGH RESISTANCE.

#### BY G. W. STEWART,

A DISCUSSION<sup>1</sup> of the measurement of current by means of the steady deflection of an electrometer needle called my attention to the fact that there is an increasing demand for a satisfactory form of a very high resistance. Rutherford, in the above reference, states that Bronson was unable to obtain sufficiently high and yet constant resistances; that tubes of xylol had too great a resistance while special carbon resistances were not sufficiently constant.

The low conductivity of carbon has naturally attracted the attention of those looking for satisfactory forms of high resistances, but the lack of constancy has always been a very great disadvantage. Longden<sup>2</sup> has published several methods of making carbon resistances which prove to be quite satisfactory, but, as he states, all the resistances increase with the time. Smoke films deposited on glass, hardened by exposure to alcohol vapor, and then covered with shellac varnish, india-rubber varnish or paraffin wax, proved to be the most satisfactory.

This note makes record of a very convenient and satisfactory form of high resistance in which carbon is utilized, and also furnishes data as to its constancy. The use of a transparent lacquer called "Zapon" in the shop of the laboratory, directed my attention to its possible combination with carbon in the formation of a permanent high resistance. The lacquer consists of soluble cotton dissolved in certain mixed solvents, the chief ingredient of which is amyl acetate. When dry, there is left a film of pyroxyline characteristics are extremely important, and the possession of them by this lacquer is the occasion of this article. It occurred to me that if lampblack were mixed with this lacquer and spread with a brush upon an insulator, a permanent and yet high resistance might be obtained. Experiment has proven this to be the case. The commercial "Germantown" lampblack and the lacquer known as "Zapon L"<sup>1</sup> were used in the experiments. The results obtained can be best described by discussing the several points of excellence of such resistances.

Convenience. — As already suggested, the resistance is obtained by spreading the mixture of lampblack and zapon upon an insulating surface. The conductivity of the films thus produced can be easily regulated by the amount of lampblack used and the thickness to which the lacquer is spread with the brush. By trial, I secured a variation in resistance from 3,000 ohms to 3,000,000 ohms with a' film approximately 3 mm. long and 2 mm. wide. In order to control the range in constructing high resistances, mixtures with varying proportions of lampblack can be kept on hand. In some experiments, resistances as high as 40,000 megohms are desired. With a film similar to the one just mentioned, it would be possible to secure this enormous resistance by a strip 0.2 mm. wide and 4 meters long. Doubtless films of less conductivity can be secured readily, thus making the length required more easily obtainable.

A further convenience is that the process of making the films is simple and easy of execution, requiring no special apparatus whatever. The forms in which the resistances can be made are unlimited, and can be determined by the purpose for which the resistance is intended. Thus far, I have experimented only with hard rubber as a base for the lacquer, and the different forms in which the rubber is readily obtainable means great convenience in the construction of such resistances. It should be stated that the sample of zapon I have used will not cling very satisfactorily to a very smooth surface, unroughened glass for example.

*Permanency.* — Films of shellac, india-rubber varnish, paraffin, and no doubt other substances have been proposed as binders for the

 $^{1\,\prime\prime}$  Zapon L  $^{\prime\prime}$  is the trade name given by the manufacturers, the Celluloid Zapon Company, Stamford, Conn.

carbon particles, the object being to make the resistance as permanent as possible. A film of pyroxyline has a decided advantage from the standpoint of permanency, for it will neither crack readily nor deteriorate.

In securing permanency care must be taken to eliminate changes in the contact between the terminals and the film. This is done by making the terminals a part of the base itself. In some of the experiments, this condition was secured by making the terminals of copper plugs screwed into the rubber plate. Longden<sup>1</sup> solved this difficulty by making the terminals of deposited silver films.

Experiments were made to test the variation of such resistances with time. Two resistances made in January were found to have varied but 3 per cent. five months later. Films of less conductivity do not age so quickly. For example, one of very much less conductivity had a value of 4.13 megohms on May 11, the day following the manufacture; on May 13 a value of 3.61 megohms; on May 15, a value of 3.45 megohms, on May 20, a value of 3.35 megohms. These figures show a variation which is at first quite large, but which grows smaller quite rapidly.

Doubtless a process of aging by baking would bring such films to a practically steady value at once. Of course a resistance which is composed of carbon particles held in position by a hardened film could in no case be as constant as a metallic resistance. It would therefore be necessary to calibrate constructed resistances from time to time, but with such occasional calibration they would remain sufficiently constant for fairly accurate work.

A variation of the resistance with the impressed voltage would not be surprising. In my first experiments, I found that the resistance decreased with increase of voltage. However, after making the terminals more a part of the base itself, as already suggested, I found the variation to be less than one half of one per cent. with a variation of voltage of 1,000 per cent. In fact, I did not detect any regular variation with voltage at all, for the sensitiveness of the apparatus would permit the detection of a variation no less than that already stated. The observations were made by connecting the resistances in series with a source of voltage and a galvatometer.

<sup>1</sup> Longden, loc. cit.

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The resistance consisted of a film about 3 mm. long and 2 mm. wide. Readings were taken with films ranging from 100,000 ohms to 3 megohms. In each case the voltage was varied at least 1,000 per cent., the actual values used depending upon the sensitiveness of the galvanometer.

The question as to the variation with voltage is an important one, in as much as in the electrometer method of measuring ionization currents, the voltage employed varies with the current to be measured. The experiments I have performed do not prove that these carbon resistances remain constant at small voltages (0.01 of a volt is sometimes used with a resistance of 30,000 megohms.) From general considerations, however, it would seem highly probable that there would be less, instead of greater, variation at lower voltages. Doubtless this form of resistance would therefore be satisfactory in the measurements of ionization currents. Apparatus with which to prove this point was not at my disposal.

As would be expected there is a variation in these carbon resistances with the temperature. A number of observations were made through small ranges of temperature, and the results show a variation of from 0.1 to 0.15 per cent. per degree centigrade. Of course this figure will depend somewhat upon the base employed for the film, and consequently must be determined for each arrangement.

The permanence of the film of pyroxyline, the fact that it can be subjected to ordinary ranges of temperature without cracking or deteriorating, would indicate that properly constructed resistances would give satisfaction for an indefinite time. Furthermore, resistances of a few megohms might easily be enclosed in sealed tubes in order to obviate any variations due to moisture.<sup>1</sup> It is believed, therefore, that this note suggests a form of high resistance which is both convenient and reasonably permanent, subjected only to very slow changes in resistance with time, and which will prove especially satisfactory where very high resistances of thousands of megohms are desired.

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<sup>1</sup> Since writing the above, I have found that these resistances increase somewhat with increase in humidity. Whether this is due to the occlusion of water vapor by the carbon or to the swelling of the pyroxyline film, has not been ascertained.

# ON PHYSICAL LINES OF FORCE IN ELECTRICAL THEORY.

#### By Fernando Sanford.

**T**N most of the discussions of electrical theory since the publication of Maxwell's great treatise the physical lines of force assumed by Faraday have played an important part. There have been various concepts as to the character of these lines of force, but apparently all who have used them have agreed in assigning to them the property of contraction lengthwise combined with another property equivalent to a repulsion at right angles to their length. Faraday apparently thought of them as elastic cords attached at their ends to unlike charges of electricity and tending to shorten and become thicker like muscle fibers. Maxwell apparently conceived of them as lines of polarized molecules imbedded in a dielectric medium, something after the order of the hypothetical Grotthus chain in electrolysis. Other writers have assumed the ether to consist of cells or molecules of positive and negative electricity and to be sheared by electric stresses so that positive electricity appears at one boundary of the stress and negative electricity at the other, while J. J. Thomson has conceived of them as some sort of vortex filaments running through, but differentiated from, the rest of the ether and terminating in a positive atom at one end and a negative atom or electron (corpuscle) at the other.

It has seemed to the present writer that the most logical and complete development of the idea of physical lines or tubes of force is to be found in the writings of Professor J. J. Thomson, and it is cate that there is any limit to the extent to which a field of electric force can be subdivided up into tubes of continually diminishing strength; the case is however different if we regard these tubes of force as being no longer merely a form of mathematical expression, but as real physical quantities having definite sizes and shapes. If we take this view, we naturally regard the tubes as being all of the same strength, and we shall see reasons for believing that this strength is such that when they terminate on a conductor there is at the end of the tube a charge of negative electricity equal to that which in the theory of electrolysis we associate with an atom of a monovalent element such as chlorine.

"This strength of the unit tubes is adopted because the phenomena of electrolysis show that it is a natural unit, and that fractional parts of this unit do not exist, at any rate in electricity that has passed through an electrolyte."

That Thomson still holds to this definition of a unit Faraday tube may be seen from his discussion of the constitution of the atom in his recent work on "Electricity and Matter." He says (Elec. and Mat., p. 133): "Now, on the electrical view of chemical combination, a univalent atom has one unit charge, if we take as our unit of charge the charge on the corpuscle; the atom is therefore the beginning or end of one unit Faraday tube: the beginning if the charge on the atom is positive, the end if the charge is negative. A divalent atom has two units of charge and therefore it is the origin or termination of two unit Faraday tubes. Thus, if we interpret the 'bond' of the chemist as indicating a unit Faraday tube, connecting charged atoms in the molecule, the structural formulæ of the chemist can be at once translated into the electrical theory."

This concept of the tube of force would seem to make the total number of Faraday tubes in the physical universe a constant, *i. e.*, one for each pair of unit positive and negative charges, and Thomson has recognized this necessity. He says (Ex. Res., 4): "These tubes also resemble the molecules of a gas in another respect, as we regard them as incapable of destruction or creation."

This would seem to mean that each unit charge of negative electricity, i. e., each electron (corpuscle) in the physical universe is indissolubly connected by a unit tube of force to its own particular positive atom, and that these unit positive and negative charges cannot change partners because to do so would oblige them to part with their own tube of force, or atomic bond, and take on a new one, and this would involve at least the temporary destruction of both tubes of force.

This plain deduction from all the possible definitions of unit physical tubes of force seems to have been overlooked by physicists who have adopted the theory, and it is inconsistent with our understanding of many of the commonest chemical phenomena. All chemical reactions are apparently dependent upon the ability of the electropositive and electronegative constituents of the reacting molecules to exchange partners.

Again, since an electron or a monovalent atom can have only one tube of force ending or beginning upon it, it can be acted upon by no other electric force whatever. An electron in any electric field is acted upon by only its own tube of force and is impelled only toward its own positive atom, and no electric force whatever can cause it to deviate from the direction of its own tube of force.

This would make it impossible for tubes of force to stretch across from one charged conductor to another, since there would be nothing at either end to hold the unit charges to their respective conductors, hence no tube of force could ever be of more than molecular dimensions.

It also follows from this assumption of unit tubes and the accepted electrical theory which goes with it that an electron can have no magnetic field of its own, since in the theory the magnetic field is due to the motion of tubes of force in a direction at right angles to their length, and an electron can have no tubes of force projecting at right angles to its direction of motion. This would seem to make necessary some other interpretation of Thomson's calculation of the electric mass of the electrons thrown off by radium in Kauffmann's experiments (Phil. Mag., 8, 331; Elec. and Mat., Chap. II.). Here Thomson has assumed a great number of Faraday tubes radiating from an electron as from a charged sphere, and by their motion at right angles to their length setting up an electromagnetic field. If it can be shown, as seems to be the case, that a single electron moving through the ether may have an electromagnetic No. 4.]

field, and hence an "electrical mass," it would seem that the idea of the unit tube of force must be abandoned or that the magnetic field must be explained by something other than the transverse motion of these tubes.

But this is not the only place where the Faraday tubes seem inadequate to explain the phenomena for which they were invented. In the attempt to explain the electromagnetic field of a current by the transverse motion of Faraday tubes it seems necessary to assume that positive electricity is leaving one plate of the battery and negative electricity the other (Ex. Res., 40; Elec. and Mat., 17) and that these opposite charges meet in the conductor where the Faraday tubes shrink to molecular dimensions. This means that one half of any electric current consists of positive charges traveling in one direction while the other half consists of negative charges traveling in the opposite direction to meet them. In other words, in any closed electric circuit one half of the conductor contains positive atoms in motion and the other half contains negative electrons moving to meet them. This seems contrary to experience, since there is no evidence that the positive atoms of a solid conductor move with the current.

On the other hand, there is strong evidence that such motion does not take place. For consider a battery composed of a zinc and an iron plate joined by a copper wire. According to the theory, a tube of force must start from a positive iron atom and a negative zinc electron and must run along between the two halves of the conducting wire carrying the iron atom at one end and the electron at the other until these meet to form a neutral iron atom in the copper wire. As we have already seen, the Faraday tube cannot release one positive atom and seize another, since in so doing it would have to exist for a finite time with a unit charge at only one end, which is contrary to the definition of all physical lines or tubes of force as well as contradictory to the third law of motion.

A similar difficulty is met with in explaining the induction of one current by another. Here the Faraday tube starting from the positive and negative ends of the primary circuit must break when it reaches the secondary circuit (Ex. Res., 41), and by taking up two unit charges from a molecule in this circuit must divide into two

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Faraday tubes, destroying as it does so the Faraday tube which originally held together the positive and negative parts of the atom which it separates. When it leaves these positive and negative parts of the atom at the other side of the secondary circuit, it must again break away from both and its free ends must unite, while a new Faraday tube comes into existence between the charged parts of the atom which now meet again in the secondary circuit.

Still another difficulty is met with in the use of the concept of Faraday tubes in the Electromagnetic Theory of Light. Here the source of light is supposed to emit Faraday tubes which move through the ether transversely to their length (Ex. Res., 42). From this point of view, a beam of plane polarized light consists of a great number of straight parallel Faraday tubes traveling through the ether at right angles to their length and with the velocity of light.

Since a beam of light has definite boundaries, these Faraday tubes must be of finite length certainly not greater than the transverse diameter of the beam, and each must carry a unit positive charge at one end and a unit negative charge at the other, *i. e.*, each Faraday tube must have a positive atom at one end and an electron at the other. This, of course, is entirely contrary to experience. Furthermore, Thomson's calculation of the electrical mass of a positive atom or electron having unit charge leads to the conclusion that this electrical mass would be infinite for charges moving with the velocity of light. Hence, from Thomson's assumptions a beam of plane polarized light consists of a very great number of Faraday tubes, each with an infinite mass at each end, moving with the velocity of light.

The above examples are cited to show the inadequacy of physical lines or tubes of force for explaining the ordinary phenomena of electricity. On the other hand, a mere mathematical line of force does not explain anything. It would seem that as long as electrical phenomena are explained by attractions between positive and negative charges either the notion of action at a distance must be revived or some kind of a physical line of force must be assumed as attached at its ends to these charges and by its contraction pulling them together.

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#### PHYSICAL LINES OF FORCE.

If, on the other hand, electric phenomena may be explained by repulsions due to a pressure exerted by the electrons upon the surrounding ether, no physical lines of force are necessary, and no properties but those required by the elastic solid theory of light need be attributed to the ether.

STANFORD UNIVERSITY, December, 1907.

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### STUDIES IN THERMO-LUMINESCENCE.

# VARIATIONS IN THE DECAY OF PHOSPHORESCENCE IN SIDOT BLENDE PRODUCED BY HEATING.

#### By C. A. PIERCE.

THE following paper deals with a quantitative study of the phosphorescence and thermo-luminescence of Sidot blende at temperatures ranging from room temperature to 300° C. The decay of the total intensity of phosphorescence of Sidot blende at ordinary temperatures, as well as the decay of individual bands has been studied by Nichols and Merritt.<sup>1</sup> No attempt has been made in the following paper to study the behavior of individual bands because of the difficulty of measuring very low intensities of light.

The apparatus used is similar in many respects to that employed by Nichols and Merritt to measure the total intensity, some necessary changes being made to adapt it to present conditions. The Sidot blende,<sup>2</sup> in powder form, was contained in a shallow tin dish which was supported on a firm base. The phosphorescence was excited by light from a Lummer mercury lamp. The powder was heated by a small electric furnace, which was mounted so as to move on a track, in order that the powder might remain undisturbed. The temperature of the powder was measured by a thermo-couple, one junction of which was imbedded in the powder, the other junction being kept at constant temperature by melting ice contained in a Dewar bulb. Another set of thermo-junctions was used to adjust the temperature of the furnace before heating the powder. There were four of these junctions, so placed that one junction came at each of the four corners of the powder dish when it was in the furnace. The intensity of the phosphorescent light was compared with a standard light by means of a Lum-

<sup>1</sup> PHYSICAL REVIEW, Vol. XXII., No. 5, May, 1906; XXIII., No. 1, July, 1906. <sup>2</sup> The powder used in these experiments was "Emanationspulver." which. while mer-Brodhun photometer. On account of the low intensity of the phosphorescent light, it was admitted directly to the double glass -prism in the photometer. Light from the center of an acetylene flame formed the standard. Colored glass was placed in front of the flame to obtain a color match, and equality of illumination in the photometer was obtained by moving the standard light.

It was found impossible to project the exciting light on to the powder without the use of a mirror. The phosphorescent light was reflected into the photometer by another mirror. A window, composed of a thin piece of mica and a piece of plate glass separated by an air space, allowed the phosphorescence to be measured when the powder was in the furnace. The mirrors were so arranged that the powder could be excited either when in the furnace or outside.

Since the observer worked alone, and in a dark room, it was necessary that the measurements be recorded automatically. The opening and closing of the shutter on the exciting lamp was recorded on a chronograph as was the beginning and end of heating. The times at which the photometer measurements were made as well as the positions of the standard lamp were recorded by pushing a button. The different keys and levers were placed so that the observer could sit with his eye at the telescope of the photometer and make all the manipulations necessary for a complete run.

Before a set of observations, the observer remained in the dark room long enough for his eyes to become sensitive to small intensities of light. At the beginning of each run, the Sidot blende was exposed to infra-red rays for one minute and then allowed to remain in darkness for five minutes before exposure to the exciting light. Nichols and Merritt have found that exposure to infra-red rays will suppress the phosphorescence almost immediately. In the present experiments it was found to be difficult, if not impossible, to obtain a source of infra-red powerful enough to destroy the thermal effect to such an extent that a temperature of about 350 degrees would not cause thermo-luminescence. But an exposure of one minute to a sixteen candle power electric lamp through thin rubber was found to be of sufficient effect to reduce the thermo-phosphorescence, even after the strongest excitation, to such an extent that it could not be measured in the photometer. The lamp was held two inches from the powder during the infra-red exposure and heated it somewhat. The wait of five minutes was sufficient, however, to allow the powder to cool off practically to room temperature.

The effect of the temperature upon the decay curve, when the Sidot blende is excited and allowed to decay at the same temperature, is shown in Fig. 1. The curves are plotted with

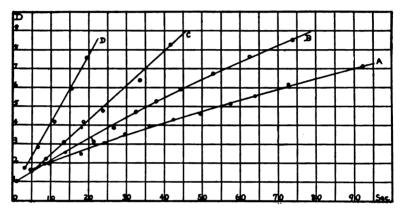


Fig. 1. Effect of temperature during excitation and decay. Excited 40 seconds. Curve A, temperature 21° C.; curve B, temperature 37° C.; curve C, temperature 60° C.; curve D, temperature 85° C.

distances of the standard lamp from the photometer screen as ordinates and time reckoned from the end of excitation as abscissæ. The ordinates D are inversely proportional to the square root of the intensity. Curves A and B are concave downward throughout, while C and D are approximately straight lines. In fact, the points on curve D indicate an upward bending.

To determine whether the decay curve becomes straight as the temperature is raised, a series of runs was made with constant length of excitation and constant temperature. The last four runs of the series are shown in Fig. 2. If the curves had been plotted with the actual times as abscissæ, they would coincide. In order that the eye may be able to distinguish readily the points on each curve, the four curves are separated by plotting curve D with the abscissæ marked on the figure and displacing the remaining curves each five seconds farther to the right. It is evident that the curves are

straight lines throughout the time of observation, but there is a possibility that the curves would show a down ward bending nearer the origin; in fact, such is believed to be the case. The conclusion, that at room temperature the observed part of the decay curve is concave downward and becomes less concave as the temperature is

raised, is substantiated by several series of curves which are not reproduced on account of lack of space.

A possible explanation of the changes in the decay curve, which occur when Sidot blende is excited at different temperatures, is deduced as follows. Let it be assumed that the law of decay for a single band in the spectrum is  $^{1}$ 

$$I = \frac{\mathbf{I}}{(a+bt)^2}$$

The decay curve of a band plotted according to this law with D

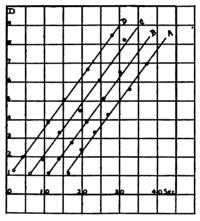


Fig. 2. Effect of temperature during excitation and decay. Excited 400 seconds. Temperature 93° C.

(equal to  $I^{-1}$ ) and t as coordinates is a straight line. Let it be assumed that the phosphorescent spectrum of Sidot blende consists of two bands, and let curves AB and CD, Fig. 3, represent the decay of these bands. The decay of the total intensity can be computed by the equation <sup>2</sup>

$$D = I^{-\frac{1}{2}} = \left[ \Sigma \frac{1}{(a+bt)} \right]^{-\frac{1}{2}},$$

and is shown in Fig. 3 by the curve OP. This curve is concave downward throughout but approaches a straight line with increase in time. From Figs. 1 and 2 it can be seen that the effect of a higher temperature is to hurry the decay. Hence the slope of the lines representing the decay of the separate bands will be greater at a

<sup>1</sup> The law proposed by H. Becquerel and tested by Nichols and Merritt. See previous

higher temperature. M.V, Fig. 3, represents the decay of the total intensity at the higher temperature. MN is concave downward throughout, but if the portion occurring within the first few seconds were not drawn, the remainder of the curve would appear to be a straight line, while under the same conditions, the curve OP would still be seen to be concave downward.

The theoretical curves in Fig. 3 represent closely the facts

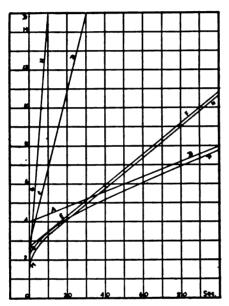


Fig. 3. AB, decay of one band at a certain temperature; CD, decay of the other band at the same temperature; OP, decay of the total intensity due to the two bands; EF, decay of the first band at a higher temperature; GH, decay of the other band at the higher temperature; MN, decay of the total intensity at the higher temperature.

deduced from Figs. I and 2. They also fit in with the deductions made by Nichols and Merritt<sup>1</sup> from their work on the decay of the total intensity of Sidot blende, namely, that the decay curve consists of two straight lines which gradually merge into one another. By changing the slopes and intercepts of the lines in Fig. 3 representing the decay of the single bands, a decay curve of the total intensity can be derived which will exactly fit the deductions mentioned above.

It is impossible to test actual curves of the decay by subtracting a straight line because there is no criterion by which the slope and intercept of the straight line can be estimated. By reference

to Fig. 3, it will be seen that the curve of total intensity does not approach closely to the straight line AB until t becomes quite large.

Other effects of the temperature at which the Sidot blende is excited can be deduced from Fig. 1. The initial intensity evi-'See previous reference.



dently increases with the temperature. The time of decay decreases as the temperature is raised. These deductions will be discussed later in connection with some other curves.

The existence of two bands in the phosphorescence spectrum of Sidot blende is suggested by the two bands in the fluorescence spectrum. Fig. 4 shows the fluorescence spectrum of the sample of Sidot blende used during these experiments when excited by a mercury lamp. The measurements were made on a Lummer-

Brodhun spectrophotometer, an acetylene flame forming the standard light. Considerable stray light was visible in the photometer despite all precautions taken to exclude it. This stray light entered through the collimator slit but was separate and distinct from the light reflected from the powder, being, apparently, uniformly distributed throughout the greater part of the spectrum. The curve AB in the figure gives an idea of the error introduced by the stray light, though no great accuracy is claimed for the exact magnitude of the error. One point in the fluorescence curve at 0.485  $\mu$ 

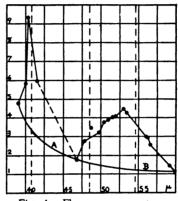
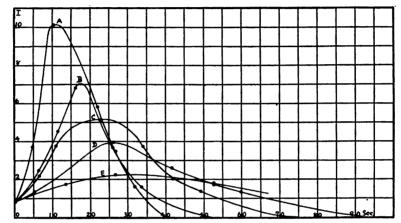
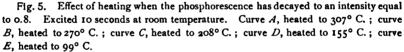


Fig. 4. Fluorescence spectrum of Sidot blende excited by a mercury lamp. Vertical broken lines show positions of the lines in the spectrum of the exciting light. Curve *AB* shows the error introduced by stray light.

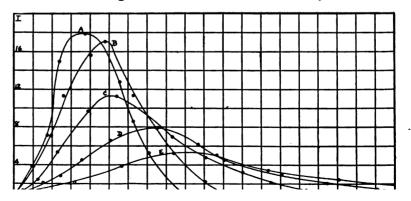
is discarded because it was taken too close to the region of a faint band in the exciting light. Despite the error due to stray light and the necessary inaccuracy of measurements made on violet light, there can be no doubt of the existence of two bands in the fluorescence spectrum, one at 0.53  $\mu$  and the other at 0.41  $\mu$ .

The effect of heating the Sidot blende after it has been excited and allowed to decay at room temperature is illustrated in Fig. 5. The curves are plotted with intensity, equal to  $D^{-2}$ , as ordinates and time measured from the moment of heating as abscissae. The effect of increased temperature is to increase the maximum intensity and to cause the maximum intensity to occur sooner after heating. Three sets of these curves are reproduced to give an idea of the accurves have been produced to zero intensity. Figs. 6 and 7 show curves similar to those in Fig. 5 at different lengths of excitation.





In the case of Fig. 5, the initial intensity immediately after excitation was somewhat greater than I = 12. The intensity was allowed





The effect of heating after excitation may be considered in one of Either it suddenly releases the energy represented by two wavs. the phosphorescence, or else it sets up some new reactions in the powder. Though the decay had reached a low intensity before heating was begun in the runs shown in Figs. 5, 6 and 7, yet at this low intensity the decay was slow; hence there may have been considerable energy still left which heating released to give the flash peculiar to thermo-luminescence. If this is the case, the areas

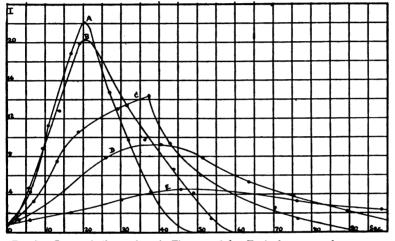


Fig. 7. Curves similar to those in Figs. 5 and 6. Excited 320 seconds at room temperature. Curve A, heated to 309° C.; curve B, heated to 266° C.; curve C, heated to 207° C.; curve D, heated to 153° C.; curve E, heated to 98° C.

between the curves in either Fig. 5, 6 or 7 and the coördinate axes ought to be equal to each other. It is impossible to get experimental data with which to draw the curves to the axis so the author projected the curves tentatively. This is not an entirely rash thing to do because a slight variation in the prolongations will affect the areas little; furthermore, while the low intensities were not measurable, one could nevertheless get some idea of the rapidity of decay by noticing how rapidly the photometer screen became dark. Fig. 8 shows the areas plotted with temperatures as abscissæ.

No attempt was made to measure the areas of the curves marked E in the figures because the approach to the axis was too slow. If the areas had been equal to each other for a given excitation, each of the curves in Fig. 8 would have been a straight line parallel to the temperature axis. With the exception of curve F, the curves show the same peculiarities but differ widely from straight lines. A plausible explanation of the shape of the curves is this. The curves of thermo-luminescence at the lower temperatures may have been projected too rapidly to the axis. This will account satisfactorily for the relative positions of the first three points in each curve in Fig. 8. The remaining point in each curve corresponds

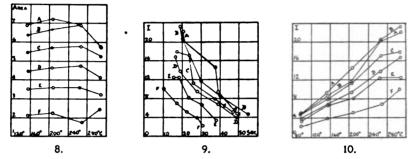


Fig. 8. Areas between the thermo-phosphorescence curves and the coördinate axes. Curve A, excited 320 seconds (from Fig. 7); curve B, excited 160 seconds; curve C, excited 80 seconds (from Fig. 6); curve D, excited 40 seconds; curve E, excited 20 seconds; curve F, excited 10 seconds (from Fig. 5).

Fig. 9. Shifting of the maximum intensity as the temperature is raised. Maximum intensity vs, time of maximum intensity measured from the beginning of heating. Curve A, excited 320 seconds (from Fig. 7); curve B, excited 160 seconds; curve C, excited 80 seconds (from Fig. 6); curve D, excited 40 seconds; curve E, excited 20 seconds; curve F, excited 10 seconds (from Fig. 5).

Each point on a curve is for a given temperature. On any curve the lowest point is for 99° C. and for the other points in consecutive order 155°, 207°, 267°, and 308° C., respectively.

Fig. 10. Increase of maximum intensity of thermo-luminescence with increase of temperature. Curve A, excited 320 seconds (from Fig. 7); curve B, excited 160 seconds; curve C, excited 80 seconds (from Fig. 6); curve D, excited 40 seconds; curve E, excited 20 seconds; curve F, excited 10 seconds (from Fig. 5).

to a temperature of about  $300^{\circ}$  C. At a temperature represented by a very dull red heat, the powder loses temporarily some of its power to phosphoresce and at a higher temperature loses this property permanently. It is possible that at about  $300^{\circ}$  C. the powder begins to change its character. If these views of the curves in Fig. 8 are correct, then the function of heating (at temperatures between  $100^{\circ}$  and  $300^{\circ}$  C.) after excitation is merely to release suddenly energy that was manifesting itself slowly.

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If this explanation of the effect of heating is correct, then it would be reasonable to expect that in the case of the curves of Fig. I the decay would be more rapid the higher the temperature, which effect has already been pointed out. The effect of greater initial intensity in Fig. I with higher temperature during excitation, if one admits that the figure indicates this, may be due to much the same causes as the effect of more rapid decay in the case of higher temperatures, but it may also be due to quite different causes. It is outside the province

of this paper to go into this question.

Fig. 9 shows the shifting of the maximum point in the curves of thermo-luminescence as the temperature is raised. No weight is given to the exact shape of the curves, the points being connected merely to aid the eye in distinguishing them. The curves are in accordance with what would be expected if the function of the temperature is to liberate suddenly the phosphorescent energy. If this is the case, the greater the temperature the quicker the energy will be liberated and the brighter the flash. The relation of maximum intensity to temperature is shown more clearly in Fig. 10.

The shape of the curves just discussed will depend upon the rate of increase of the temperature of the

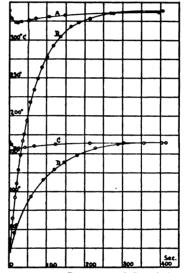


Fig. 11. Curves A and C, variation in temperature of furnace when the powder is put in. Curves B and D, increase in temperature of the powder. Curves A and B do not become identical because they were not taken simultaneously and the temperature changed slightly between the two runs.

powder. Two curves were taken in the region of each of the temperatures used to show the increase of temperature of the powder and the variation in temperature of the furnace when the powder is heated. Fig. 11 shows the curves for two of the temperatures. The conclusion drawn from the complete set of curves is that indicated by Fig. 11: the powder reaches a constant temperature in a constant time independent of the temperature. The periods of the two galvanometers used in the temperature measurements were too short to affect the shape of the curves appreciably.

This method of heating possesses several advantages. The temperatures are known and can be accurately reproduced as many times as desirable. Further, the gradual heating allows the flash to be followed in the photometer. For some other work a strip of platinum which supported a thin layer of the powder was heated by passing an electric current through the strip. The flash in this case occurred too rapidly to be followed, the maximum intensity being the only measurement possible.

It is not easy to estimate the effect of gradual heating as compared with more nearly instantaneous heating. The outside layer

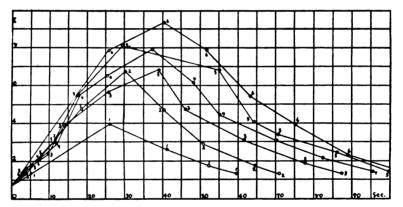


Fig. 12. Effect of varying the length of excitation. The length of excitation and the temperature of the furnace are as follows:

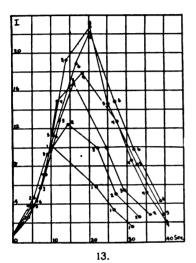
Curve 6, 320.0 se	ec., 153.0° C.	Curve 3, 40.0 sec., 155.5° C.
" 5, 160.0	•• 155.5°	" 2, 19.9 " 155.5°
" 4, 80.1	•• 155.5°	" 1, 10.0 " 155.0°

of the powder is subjected to the temperature of the furnace which does not vary widely. It is only the inside layers which are heated as slowly as the curves in Fig. 11 indicate. It is not believed that any material change is introduced in the relation of the various curves, though the actual form of the curves may be changed more or less.

The effect of varying the length of excitation is brought out in Figs. 12 and 13. As in previous curves, the phosphorescence was



excited at room temperature and allowed to decay to I = 0.8 before heating. The points are joined by straight lines to aid the eye in following the individual curves. Two effects are noticeable at a glance. The maximum intensity increases with excitation and is shifted to the right, *i. e.*, comes at a later time. The effect of saturation is also shown. This is brought out more clearly in Fig. 14



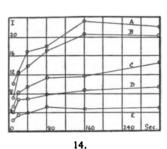


Fig. 13. Curves similar to Fig. 12. Effect of varying the length of excitation. The length of excitation and the temperature of the furnace are as follows:

Run	6,	320.1	sec.,	309 ° C.
"	5,	159.9	"	308°
**	4,	80.2	"	308°
**	3,	39.9	"	308°
"	2,	20.0	"	309°
"	1,	10.0	"	307°

Fig. 14. Saturation effect.  $I_H$  vs. length of excitation. Curve A, temperature 308° C.; curve B, temperature 267° C.; curve C, temperature 207° C.; curve D, temperature 155.5° C.; curve E, temperature 98° C.

To get the maximum point in each run, smooth curves, not shown in the figures, were drawn through the different points. These curves show that increasing the excitation beyond a certain length does not increase the energy manifested as thermo-luminescence. That saturation takes place is further shown by the time that luminescence lasts. Figs. 12 and 13 show that the duration of luminescence has about reached a maximum. The areas included between the curves and the coördinate axes also show that further increase with increased excitation is limited. The shifting of the maximum intensity resembles an inertia effect; the longer the excitation the longer it takes the temperature to produce the maximum thermo-effect.

The effect of delay between the end of excitation and the beginning of heating is shown in Fig. 15.

While Fig. 15 gives a clear idea of the relation of the different curves of thermo-luminescence to the curve of decay of phos-

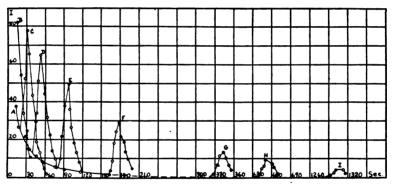


Fig. 15. Effect of delay in heating. Time measured from the end of excitation. Excited 320 seconds at room temperature. Temperature of furnace  $303^{\circ}$  C. Curve A, decay at room temperature. The time between the end of excitation and the beginning of heating is as follows:

Curve	<i>B</i> , 2.5 sec.	Curve F,	162.0 sec.
**	C, 21.4 "	" G,	321.6 ''
"	D, 41.3 "	" Н,	631.8 ''
**	E, 81.1 ''	" <i>I</i> ,	1280.0 "

phorescence at room temperature, Fig. 16 gives a better idea of the relation between the different curves of thermo luminescence. Two other sets of these runs under different conditions are given in order that the general characteristics of the curves may be noted.

The last three sets of curves show shifting of the maximum intensity as the delay in heating is increased. The shifting is in the same direction on that national in the same direction of the same di

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case of short delay in heating or short excitation. Another point is that at any given excitation and temperature, the curves apparently coincide after a certain time. Out of nine sets of curves, the set in Fig. 16 is the only one that does not exhibit constancy in the time required for the curves of thermo-luminescence to flash out and decay. It is probable that Fig. 16 would show the same

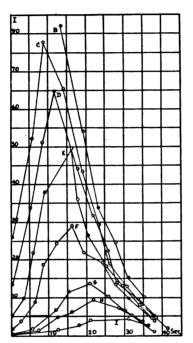


Fig. 16. Effect of delay in heating. Time measured from beginning of heating. Same runs as in Fig. 15.

effect if the curves had been followed to an intensity as low as in the other cases.

Table I. sums up the time for the flash in the case of nine sets of curves gotten under varying conditions. Table I. is naturally very inaccurate because, as seen in Figs. 16, 17 and 18, which are included in the nine sets, the curves do not exactly coincide at any point.

Fig. 19 gives a summary of the nine sets of curves showing the decrease in maximum intensity with delay in heating. Curve G, Fig. 19, is taken from Fig. 15.

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Excite	d 10 :	sec.	Temp	. of f	urnac	e 94º C.	Time	: fo <b>r</b> i	ntensit	y to r	each	I = 1.25	60 s	iec.
44	10	**	**	**	**	200°	**	""	46	"	"	"	45	"
44	10	**	64	**	**	<b>30</b> 2°	46	" "	46	"	**	"	32	**
**	40	**	**	**	**	<b>92°</b>	**	**	**	"	44	I=2.5	100	44
**	40	"	"	**	**	200°	**		"	" "	" "		80	"
**	40	66	**	**	**	300°	"	**	**	**	66	"	37	"
	320	**	**	**	**	93°	"	**	"	"	"	"	120	"
64	320	"	**	**	44	202°	**	44	**	• 6	**	"	75	"
44	320	**		66	44	303°	44		"	46	"		40?	"

TABLE I.

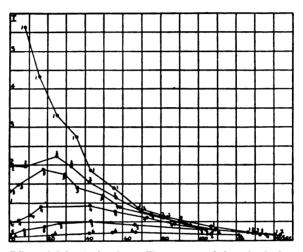


Fig. 17. Effect of delay in heating. Time measured from beginning of heating. Excited 320 seconds at room temperature. Temperature of furnace 93° C. The time between the end of excitation and the beginning of heating is as follows:

Curve 1, 2.0 sec.	Curve 4, 81.5 sec.
·· 2, 21.9 ··	<b>''</b> 5, 162.0 ''
" 3, 41.5 "	<b>"</b> 6, 332.0 <b>"</b>

Fig. 20 shows the maximum intensity in the nine sets of curves plotted against the time of the maximum measured from the beginning of heating. The characteristic shifting of the maximum in the case of delay in heating is clearly seen.

In Fig. 21 is shown the maximum intensity plotted against length of excitation for the nine sets of curves. These curves are similar to those shown in Fig. 14 but cover a larger range of conditions. The straight lines in the figure tend to be misleading for they indicate that the saturation is less complete the shorter the time inter-



vening between excitation and heating. But if one takes Fig. 14 as a model, curves can be drawn through the points in Fig. 21 show-

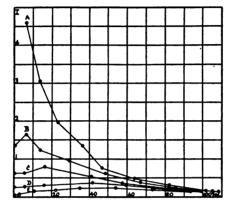


Fig. 18. Curves similar to Fig. 16. Excited 40 seconds at room temperature. Temperature of furnace 94° C. The time between the end of excitation and the beginning of heating is as follows: Curve A. 1.9 sec.

Curve	: A,	1.9	sec.
"	В,	22.1	"
"	С,	42.1	44
"	D,	82.6	"
"	Ε,	162.1	" "

ing that the saturation is probably as complete for one time of delay as another.

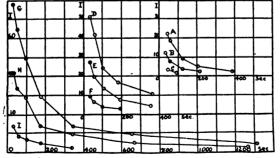


Fig. 19. Decrease in maximum intensity with delay in heating. The coordinates are

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C. A. PIERCE.

Fig. 22 shows the relation between maximum intensity and temperature for the nine sets of runs. These curves correspond to those shown in Fig. 9. In some of the curves but one point can

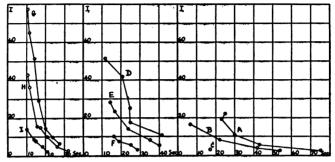


Fig. 20. Maximum intensity vs. time of maximum intensity measured from the beginning of heating. For description of curves see Fig. 19.

be given, the other runs showing no measurable intensity or else no maximum. The relation between the maximum intensity and

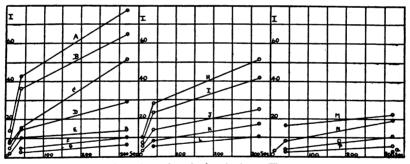


Fig. 21. Maximum intensity vs. length of excitation. The temperature of the furnace and the time between the end of excitation and the beginning of heating are as follows:

Curve	e A, 3	02° C.,	, 21.6	sec.		Curve	: H,	200° C.,	21.9	sec.
**	Β,	••	41.7	"		**	Ι,	66	41.5	"
**	С,	**	81.4	"		**	<i>J</i> ,	"	81.6	"
"	D,	"	161.6	**		**	K,	" "	161.8	"
"	Ε,	"	321.0	"		**	L,	**	321.7	"
"	F,	"	636.0	"						
"	G,	"	1155.0	"						
			Curve	М,	93° C.,	21.5	sec.			
			" "	N,	**	41.8	"			
			**	0,	**	82.0	"			
			"	Ρ,	<b>٠</b> ٩	162.0	**			
			"	Q,	* *	322.0	"			



the temperature, beyond the fact that the intensity increases with the temperature is not clear.

In many of the figures given, it is probably unwise to lay too much stress upon the exact shape of the curves.

In the first part of this paper mention was made of the existence of two bands in the phosphorescence spectrum of the sample of Sidot blende used in this study when excited by a mercury lamp. If there are two bands, it is natural to expect some indication of their existence in the curves of thermo-luminescence. Referring to Figs. 16

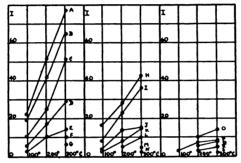


Fig. 22. Maximum intensity vs. temperature of furnace. The length of excitation and the time between the end of excitation and the beginning of heating are as follows:

Curve	А,	320 sec.,	21.7	sec		Curve	H, 4	Ю sec.,	22.1	sec.
**	В,	"	41.3	"		**	Ι,	" "	41.8	"
"	С,	* *	81.3	"		**	Γ,	**	81.6	"
"	D,	**	162.0	"		"	K,	"	161.9	"
"	Ε,	**	321.8	"		**	L,	"	321.9	"
"	F,	"	631.8	" "		**	М,	" "	642.0	**
"	G,	**	1280.0	"		**	Ν,	"	1230.0	"
			Curve	о,	10 sec.,	21.8	sec.			
			**	Ρ,	"	41.7	"			
			" "	Q,	"	81.7	"			
			**	R,		161.4	"			
			"	S,	**	319.5	"			

and 17, there will be found evidence of two bands. After the intensity has reached a maximum, it falls off rapidly at first, then there is an indication of a slowing up in the decay followed by relatively rapid decay. Whether there is a complete bending back in any of the curves cannot be stated because the points are too far apart. Whether a complete bending back is possible depends on the relative intensities of luminescence of the two bands and the relative rapidity of decay. It has not seemed advisable to search for more certain indications of two bands in the thermo phosphorescence because of the difficulty of increasing the number of observations taken in a given time. In a paper to follow this, curves will be shown in the case of Balmain's paint, which decays slowly enough to be more completely studied. This substance has two bands in its phosphorescence spectrum and the curves of thermo-luminescence show two maxima under certain conditions of excitation, temperature, and delay in heating. It is possible that the study of this substance has somewhat distorted the author's vision in the case of Sidot blende, but the fact that the indications of a change in the decay of thermo-luminescence correspond in time for the different curves points toward the existence of two bands.

The author wishes to express his obligations to Professor Merritt for suggesting this line of investigation and for other suggestions during the progress of the work.

PHYSICAL LABORATORY OF CORNELL UNIVERSITY.



#### PROCEEDINGS

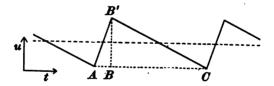
#### OF THE

# American Physical Society.

# How Does a Violinist Control the Loudness of His Tone?<sup>1</sup>

#### BY HARVEY N. DAVIS.

A CCORDING to the Helmholtzian theory of the violin string, the motion of the part of the string in contact with the bow can be represented by a simple zigzag line like that in the accompanying figure, if values of the time t are plotted as abscissæ and the corresponding displacements u of the point bowed as ordinates. B'C represents that part of the motion which is in the direction of the bowing, and during it the string is sticking fast to the bow and moving with its velocity. The ratio



of the time-interval BC to the period AC is determined solely by the distance of the point bowed from the ends of the string; if this point is one seventh of the length of the string from the bridge, BC is six sevenths of AC, and so in general. Therefore the amplitude BB' is wholly determined when the position and speed of the bow are given. When the bow is brought nearer the bridge the amplitude BB' increases, and it is easy to prove that the amplitude at the center of the string increases still more, so that the sound should be louder than before. This is indeed the case, as every violinist knows. If, however, it be desirable not to move the bowing point, then, on the Helmholtzian theory, the amplitude of the string and the loudness of the sound produced are wholly determined by the speed of the bow, and are not affected by a change in its pressure — a conclusion that does not seem to be in agreement with experience.

An explanation of this discrepancy can be based on certain results

cannot be maintained, and that this critical pressure varies very nearly as the bowing speed. It can be considerably exceeded without changing the nature or magnitude of the vibration, but a violinist would ordinarily use as small a pressure as his bowing speed at the moment would allow, both because of the scratching which too great a pressure causes, and to avoid undue fatigue. Therefore, even if loudness is determined by bowing speed alone, a greater bowing speed would always be accompanied by a greater pressure, and this would seem to be the cause of the loud tone. This tends to mask the real issue which is whether loudness increases with pressure at a constant bowing speed; but even when it is allowed for, experience seems to be against the Helmholtzian theory.

The author is therefore led to believe that the actual motion of a violin string is usually not of the normal Helmholtzian type, but of the sort described to the Society a year ago as corresponding to light bowing. It is characteristic of this sub-critical region that diminishing the pressure of the bow carries the ordinary straight line form continuously over into one from which the overtones have entirely disappeared, the amplitude of the fundamental being also somewhat reduced. With the special apparatus previously described to the Society, it is possible, when the string is bowed at its middle point, to reduce the energy of its motion to barely half the normal value, and when the bow is near one end, the reduction is much greater. Since the variations in loudness may, for various reasons, be expected to be even greater than the variations in the energy of the string itself, there should be no difficulty in accounting for the magnitude of the effects actually observed. This explanation obviously requires that the quality of the tone should change when its loudness is varied at constant bowing speed, and this seems to be the case, although the effect is not as marked as might be expected.

The author hopes to be able to determine the limits of the sub-critical region for an actual violin, and to compare with them certain observations already obtained of the pressures ordinarily used. In the meantime he will be grateful for any information which may help either to confirm or to disprove these conclusions.

THE JEFFERSON PHYSICAL LABORATORY, CAMBRIDGE, MASSACHUSETTS.

# THE SPECTRUM OF CALCIUM.<sup>1</sup>

#### BY JAMES BARNES.

THE paper considers the charges produced in the intensity and distribution of light in the lines of the calcium spectrum obtained from an arc between metallic electrodes in air at atmospheric pressure

<sup>1</sup>Abstract of a paper presented at the Chicago meeting of the Physical Society, December 30, 1907, to January 2, 1908.



and at lower pressures with varying current-strength. The results can be explained as a density effect rather than a temperature one.

The new triplets found by Saunders in a copper arc moistened with CaCl, appear very clearly and sharp when the arc is produced in a vacuum with a current of 12 amperes.

Many attempts were made to obtain true double reversals of the H and K lines with a steady arc but without success. False multiple and double reversals appear in some of the other lines.

# THE RESISTANCE TEMPERATURE COEFFICIENT AND THE COEFFICIENT OF EXPANSION OF LAMPBLACK.<sup>1</sup>

#### BY G. W. STEWART.

WITH the exception of the diamond and charcoal, carbon in its various forms conducts electricity metallically. Its resistance temperature coefficient is, however, negative. This paper accounts for the apparent negative coefficient by assuming the changes in resistance to be due to the expansion of the particles of carbon.

Assuming this explanation to be the correct one, experiments were performed to obtain the coefficient of expansion of carbon. The carbon used was in the form of films made of commercial lampblack and a lacquer called "zapon L." The apparent resistance temperature coefficient of the films and the effect of the expansion of the hard rubber base upon which the films were placed were measured, and the actual coefficient of expansion of the carbon particles was computed. The result obtained shows the coefficient of carbon in the form of lampblack to be about 0.0002, which is from ten to thirty times that of the pure metals.

A New Method for Determining the Smallest Interval of Time Perceptible by the Ear.<sup>1</sup>

#### BY BRUCE V. HILL.

THIS experiment has been tried many times but, having the apparatus described in a previous paper for the measuring of short intervals of time in condenser discharge at hand, the author with Professor J. E. Boodin, of the University of Kansas, thought it of interest to repeat it.

Through the primary of a small induction coil were connected two parallel circuits, each under the control of one of the keys to be liberated by the falling weight. The secondary of the coil was connected through a cable, to a telephone receiver in a distant room, signals being arranged between the subject in this room and the operator of the falling weight

<sup>1</sup>Abstract of a paper presented at the Chicago meeting of the Physical Society, December 30, 1907, to January 2, 1908.

apparatus. The parallel resistances were adjusted till the subject was unable to distinguish which of the two circuits was opened.

A series of stimuli were then given, successive and simultaneous impulses being given at random, till the answers of the subject were as often incorrect as correct. Results as low as .00144 second were thus obtained. This discrimination was evidently not of an interval but rather of duration or of a quality difference. The estimate of interval proper is difficult to make, as so much depends upon the candor of the subject. The interval thus found was .007 second, which agrees well with that found by former experimenters.

The secondary of the induction coil was connected to the moving part of an oscillograph, and the beam of light made to fall upon a cylinder covered with a sensitive film and rotated at a high speed by a motor. With an interval of .0015 the oscillograph showed two distinct impulses.

CHICAGO, ILLINOIS, November 15, 1907.

#### A RELATION OF MASS TO ENERGY.<sup>1</sup>

BY DANIEL F. COMSTOCK.

IN the paper of which this is an abstract it is shown that the momentum of any purely electric system having any internal motions and constraints, but possessing on the whole a kind of average symmetry, is given by the expression

$$M = \frac{2 W_T v}{V^2 \left[1 + \left(\frac{v}{V}\right)^2\right]}.$$

Here M is the momentum of the system, (v) its velocity as a whole, V the velocity of light and  $W_T$  the part of the total electromagnetic energy which is represented by the components of the electric and magnetic forces which lie perpendicular to the direction of motion of the system. This is a highly general result and is obtained by a method involving the generalized constraints of the system.

When the second order of the ratio v/V may be neglected,  $W_r$  is equal to two thirds the total electromagnetic energy (W) of the system (because of the average symmetry before mentioned), and hence we have

$$Mass = \frac{4}{3} \frac{I}{V^i} W.$$

This gives the electromagnetic mass of the system in terms of its total energy content.

<sup>1</sup>Abstract of a paper presented at the Chicago meeting of the Physical Society, December 30, 1907, to January 2, 1908.



If the electrical theory of matter be accepted this result applies to the mass of any piece of matter and we have the mass proportional to the total contained energy.

It is shown that if this hypothesis is accepted the irregularities which exist in the table of atomic weights are in harmony with the evolutionary theory of the elements.

Also on this basis gravitation must be considered as acting between quantities of confined energy and not between masses in any other sense.

#### NEW BOOKS.

Das Problem der Schwingungserzeugung mit besonderer Berücksichtigung schneller elektrischer Schwingungen. By Dr. H. BARKHAUSEN. Pp. 113. Leipzig, S. Hirzel, 1907.

This is a timely book on a live topic. The production of undamped electrical oscillations of high frequency is the principal theme of the book, but the author approaches the subject from the broadest theoretical standpoint; first deducing a series of propositions defining the conditions under which it is possible to derive a sustained periodic current from an aperiodic energy-source, and then discussing in systematic order the various means by which these conditions may be met. Each case is considered theoretically and illustrated by some form of actual apparatus which fulfills the prescribed conditions and affords a more or less practical solution of the problem. The treatment is general enough to include such familiar devices as the alternating-current dynamo and the statical influence machine, the former being regarded as a current system in which the variables are self- and mutual induction, the latter illustrating the case of variable capacity. The old problem of the telephone relay enters as another phase of the subject, where a periodic current already existing is to be strengthened by the addition of energy from an outside aperiodic source.

The center of interest, however, is in the discussion of the singing arc, to which a large part of the book is devoted. The three types of oscillation which this apparatus may execute are described with admirable clearness and illustrated by diagrams derived from the author's equations. It is interesting to note how closely these purely theoretical curves agree with the oscillograph records obtained by Blondel under conditions similar to those here assumed.

A final chapter on the various types of mechanical oscillations and their analogy to the corresponding electrical phenomena will greatly assist the reader in grasping the physical meaning of the generalizations by giving a clearer mental picture of the phenomena involved.

The book is particularly welcome at this time when undamped oscillations are the order of the day in wireless telegraphy and telephony, and all sorts of possible and impossible oscillators are appearing. Even to those not especially interested in the subject it is well worth the reading, and the author's clear logic and often original viewpoint are refreshing and full of suggestiveness. No attempt is made to furnish a complete review of the art. The object is rather to correlate and systematize the diverse and scattered contributions to the subject, and in this the author has been eminently successful. FREDERICK K. VREELAND.



### THE

# PHYSICAL REVIEW.

# EXPERIMENTS ON THE INDUCTION OF CURRENTS IN CYLINDRICAL CORES.

#### BY ROY T. WELLS.

INTRODUCTION AND OBJECT.

CONSIDER two simple electric circuits of mutual inductance M, one, the primary, having resistance  $R_1$  and inductance  $L_1$ , the other, the secondary, having resistance  $R_2$  and inductance  $L_2$ . If a harmonic electro-motive force of frequency  $f = p/2\pi$  is impressed on the primary and the secondary is closed, the secondary current will react on the primary circuit, changing its effective resistance and inductance from  $R_1$  and  $L_1$  to <sup>1</sup>

$$R' = R_1 + \frac{R_2 M^2 p^3}{R_2^2 + L_2^2 p^2} \quad \text{and} \quad L' = L_1 - \frac{L_2 M^2 p^3}{R_2^2 + L_2^2 p^2}.$$
(1)

Equations (1) are derived from the equation

$$E = I \left[ L_1 i p + R_1 + \frac{M^3 p^3 (R_2 - L_2 i p)}{R_2^2 + L_2^2 p^3} \right],$$

where E and I are either the maximum or the effective values of the impressed electro-motive force and the primary current and  $i = \sqrt{-1}$ .

The impedance of the primary circuit becomes

$$Z = \frac{E}{I} = L_1 i p + R_1 + \frac{M^3 p^3 (R_2 - L_2 i p)}{R_2^2 + L_2^3 p^2},$$
 (2)

where the real part,

<sup>1</sup> See Webster, Electricity and Magnetism, p. 481.



$$R_1 + \frac{R_2 M^3 p^3}{R_2^2 + L_2^2 p^2},$$

is the effective resistance and the imaginary part,

$$ip\left(L_1 - \frac{L_2 M^2 p^2}{R_2^2 + L_2^2 p^2}\right),$$

is *ip* times the effective inductance.

If the primary circuit is a uniformly wound coil, with straight axis and circular cross-section, and the secondary is a circular cylinder of metal or other conducting material, inside of and coaxial with the coil and of the same length, the reactions of the secondary currents will be of the same character as in the case of two simple circuits. If the coil is so long in comparison to the radius of its section that the magnetic field along any line parallel to the axis may be regarded as uniform throughout its length, then each tube of infinitesimal thickness in the core, co-axial with the coil, will be the seat of a current sheet flowing around it, and producing a magnetic field in its interior. Every current element will flow in a plane normal to the axis. The magnetic field in any tube will be that due to the resultant effect of the coil current and all core currents in tubes outside it. Both the magnetic field and the current will be uniform over any tube, but will vary from tube to tube in intensity and phase, that is, they will be functions of only one geometrical parameter, the distance of the tube from the axis.

If a harmonic electro-motive force is impressed on such a coil, the core current reactions will oppose the setting up of the coil current for a time, but very soon a steady state will be reached in which there will be a harmonic current in the coil and a harmonic variation of strength of current and magnetic field in each tube of the core. These tubes are infinite in number and the system is one with an infinite number of degrees of freedom.

The reactions of the core currents will change the effective

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- H = intensity of the magnetic field.
- I = coil current.
- q =density of core current.
- $\rho$  = resistivity of the core.
- $\mu$  = permeability of the core.
- r = distance from the axis of the coil.
- R =resistance of the coil.
- c = radius of the core.
- $L_0 =$ inductance of the coil  $= L_1 + L_2$  where
- $L_1$  = inductance due to the space occupied by the core and
- $L_{1}$  = inductance due to the space outside the core.
  - l =length of the coil and the core.
- n = number of turns of the coil per centimeter length.
- Z =impedance of the coil.
- f = frequency in cycles per second of the electro-motive force impressed on the coil.

 $p = 2\pi f$ .

A tube of thickness dr has flowing in it a current qdr per centimeter of length. This produces inside the tube the magnetic field  $4\pi qdr$ . Just outside the tube H is less by the part of H within that is due to the current in the tube, or the decrease in H in the radial distance dr is

$$- dH = 4\pi q dr. \tag{3}$$

If e is the electric force in the tube, the electro-motive per centimeter circumferentially, then by Ohm's law

$$\boldsymbol{e} = \rho q, \tag{4}$$

*e* being entirely due to the change in the magnetic induction within the tube.

From (3) and (4) we have

$$e = -\frac{\rho}{4\pi} \frac{dH}{dr}.$$
 (5)

force around the tube, or to the line integral of e around it, that is,

$$2\pi re = -\frac{d}{dt} \int_0^{\infty} \mu H 2\pi r dr.$$

From this equation and (5) we have

$$e = -\frac{\rho}{4\pi} \frac{dH}{dr} = -\frac{1}{2\pi r} \frac{d}{dt} \int_0^{\infty} \mu H 2\pi r dr.$$

Lord Rayleigh has shown<sup>1</sup> that if the magnetic field intensity is very small,  $\mu$  is nearly constant for iron, and  $\mu$  is of course constant for any non-magnetic core. If we assume  $\mu$  as constant then

$$\frac{\rho}{4\pi} \frac{dH}{dr} = \frac{\mu}{r} \int_0^r \frac{dH}{dt} r dr,$$
$$r \frac{dH}{dr} = \frac{4\pi\mu}{\rho} \int_0^r \frac{dH}{dt} r dr.$$

or

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Differentiating and dividing both sides by r we have

$$\frac{1}{r}\frac{d}{dr}\left(r\frac{dH}{dr}\right) = \frac{4\pi\mu}{\rho}\frac{dH}{dt}.$$
(6)

If the electro-motive force impressed on the coil is harmonic then H is harmonic at every point and we may put

 $H = e^{\operatorname{pit}} U$ 

where U is a function of only the geometrical parameter r, and hence

$$\frac{dH}{dt} = ipH = ipe^{pit}U.$$

Also since

$$\frac{1}{r}\frac{d}{dr}\left(r\frac{dH}{dr}\right)$$

involves operations by r only, we have

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 $\frac{4\pi\mu}{\rho}i\rho\epsilon^{\text{pit}}U = \epsilon^{\text{pit}}\frac{1}{r}\frac{d}{dr}\left(r\frac{dU}{dr}\right)$ 

or

$$\frac{1}{r}\frac{d}{dr}\left(r\frac{dU}{dr}\right) = \frac{4\pi\mu}{\rho}i\rho U = -k^2 U,$$
(7)

where

$$-k^2 = \frac{4\pi\mu i\rho}{\rho} = ix$$
, putting  $x = \frac{4\pi\mu\rho}{\rho}$ 

The equation

$$\frac{1}{r}\frac{d}{dr}\left(r\frac{dU}{dr}\right) = -k^2U$$

is satisfied by putting for U the Bessel's function

$$U = C f_0(kr) = C \left( 1 - \frac{k^2 r^2}{2^2} + \frac{k^4 r^4}{2^2 4^2} - \frac{k^6 r^6}{2^2 4^2 6^3} + \cdots \right), \tag{8}$$

where C is any constant. This value of U also satisfies the physical condition of being uniform, finite and continuous over the core, from r = 0 to r = c, and is accordingly the solution desired.

We have

$$k = \sqrt{-ix}$$

hence

$$J_0(kr) = J_0(r\sqrt{-ix}),$$

 $= I + \frac{ixr^2}{2^2} - \frac{x^2r^4}{2^24^2} - \frac{ix^3r^6}{2^24^26^2} + \frac{x^4r^8}{2^24^26^28^2} + \frac{ix^5r^{10}}{2^24^26^28^{2}10^3} \cdots = M(r) + iN(r),$ where

$$M(r) = 1 - \frac{x^2 r^4}{2^2 4^2} + \frac{x^4 r^8}{2^2 4^2 6^2 8^2} - \frac{x^6 r^{12}}{2^2 4^2 6^2 8^2 10^2 12^2} + \cdots$$

$$N(r) = \frac{x r^2}{2^2} - \frac{x^3 r^6}{2^2 4^2 6^2} + \frac{x^5 r^{10}}{2^2 4^2 6^2 8^2 10^2} - \frac{x^7 r^{14}}{2^2 4^2 6^2 8^2 10^2 12^2 14^2} + \cdots$$
(9)

and thus  $H = Ce^{\text{pit}} [M(r) + iN(r)].$ 

At the outside of the core r = c. Here, and from here out to the inside of the coil, H is uniform and determined by the coil current I. At the surface of the core then

$$H_{c} = 4\pi nI = Ce^{\text{pit}} [M(c) + iN(c)],$$

$$I = \frac{Ce^{\text{pit}} [M(c) + iN(c)]}{4\pi n}.$$
(10)

or

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The inductance  $L_2$  due to the space outside the core is not affected by the core currents. If there are no core currents, the inductance  $L_1$  due to the space filled by the core is  $L_1 = 4\pi^2 n^2 c^2 \mu l$ . When the core currents flow the number of linkages of turns of the coil with unit tubes of induction in this space is

$$nl\mu\int_0^\infty H2\pi rdr,$$

where H is the total field due to the coil and core currents. When E is impressed on the coil a current I will flow. E may at any instant be divided in three parts. The first, RI is used to overcome the ohmic resistance of the coil; the second,

$$L_2 \frac{dI}{dt} = (L_0 - L_1) \frac{dI}{dt}.$$

to overcome the counter electro-motive force due to the change of induction in the space outside the core; and the third,

$$\frac{d}{dt}\Big(nl\mu\int_0^\infty H2\pi rdr\Big),$$

to overcome the similar counter electro-motive force due to the change of induction in the core space. We have then

$$E = RI + (L_0 - L_1) \frac{dI}{dt} + 2\pi n l \mu \int_0^c \frac{dH}{dt} r dr,$$
  
or by (6)  
$$E = RI + (L_0 - L_1) \frac{dI}{dt} + \frac{\rho n l}{2} \int_0^c \frac{d}{dr} \left( r \frac{dH}{dr} \right) dr$$
$$= RI + (L_0 - L_1) \frac{dI}{dt} + \frac{\rho n l c}{2} \left[ \frac{dH}{dr} \right] (r = c).$$
<sup>(11)</sup>

Now

$$\frac{dH}{dr} = Ce^{\text{pit}} \frac{d}{dr} \left[ M(r) + iN(r) \right].$$

Let us put M'(r) for

$$\frac{dM(r)}{dr} = -\frac{x^2r^3}{2^24} + \frac{x^4r^7}{2^24^26^28} - \frac{x^6r^{11}}{2^24^26^28^{2}10^212} + \cdots;$$
  
N'(r) for

$$\frac{dN(r)}{dr} = \frac{xr}{2} - \frac{x^3r^5}{2^24^26} + \frac{x^5r^9}{2^24^26^28^210} - \frac{x^7r^{13}}{2^24^26^28^210^212^214} + \cdots$$

M for

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;

No. 5.]

$$\mathcal{M}(c) = \mathbf{I} - \frac{x^{2}c^{4}}{2^{2}4^{2}} + \frac{x^{4}c^{5}}{2^{2}4^{2}6^{2}8^{2}} - \frac{x^{6}c^{13}}{2^{2}4^{2}6^{3}8^{2}10^{2}12^{3}} + \cdots;$$

N for

$$N(c) = \frac{xc^3}{2^2} - \frac{x^3c^6}{2^2 4^2 6^3} + \frac{x^5c^{10}}{2^3 4^2 6^2 8^3 10^2} - \frac{x^7c^{14}}{2^3 4^2 6^2 8^2 10^2 12^3 14^3} + \cdots;$$

M' for M'(r) when r = c giving

$$M' = -\frac{x^2 c^3}{2^2 4} + \frac{x^4 c^7}{2^2 4^2 6^2 8} - \frac{x^4 c^{11}}{2^2 4^2 6^2 8^3 10^3 12} + \cdots;$$

N' for N'(r) when r = c giving

$$N' = \frac{xc}{2} - \frac{x^3c^5}{2^34^36} + \frac{x^5c^9}{2^24^{2}6^{2}8^{2}10} - \frac{x^{7}c^{13}}{2^24^{2}6^{3}8^{3}10^{3}12^{3}14} + \cdots$$

We get then from (11)

$$E = RI + (L_0 - L_1)\frac{dI}{dt} + \frac{\rho nlc}{2} C e^{\text{pit}}(M' + iN').$$
(12)

Since now *E* is harmonic it may be represented by  $E = Ae^{pit}$ , and *I* will be harmonic and may be represented by  $I = Be^{pit}$ , or as in (10) by

$$\frac{Ce^{\operatorname{pit}}(M+iN)}{4\pi n} \quad \text{and} \quad \frac{dI}{dt} = i\rho Be^{\operatorname{pit}} = i\rho I.$$

The impedance of the coil is Z = E/I and we get

$$Z = \frac{RI}{I} + \frac{(L_0 - L_1)iPI}{I} + \frac{\rho n lc C e^{pit} (M' + iN') 4\pi n}{2 C e^{pit} (M + iN)}$$
$$= R + (L_0 - L_1)ip + 2\pi n^2 \rho lc \frac{M' + iN'}{M + iN}$$
$$= R + (L_0 - L_1)ip + \frac{L_1 \rho}{2\pi\mu c} \frac{MM' + NN' + i(MN' - M'N)}{M^2 + N^2} \cdot (13)$$

By analogy with (2) we may put the real part of Z equal to the effective resistance

$$R' = R + \frac{L_{1}\rho}{2\pi\mu c} \frac{MM' + NN'}{M^{2} + N^{2}}.$$
 (14)

and the imaginary part, divided by ip, equal to the effective inductance

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$$L' = L_0 + L_1 + \frac{L_1 \rho}{2\pi \mu c \rho} \frac{MN' - M'N}{M^2 + N^2} = L_0 - L_1 \left( 1 - \frac{\rho}{2\pi \mu c \rho} \frac{MN' - M'N}{M^2 + N^2} \right).$$
<sup>(15)</sup>

The absolute value of the impedance is

$$Z = (R'^{2} + L'^{2}p^{3})^{\frac{1}{2}} = \left[ R^{2} + (L_{0} - L_{1})^{2}p^{2} + \left(\frac{L_{1}\rho}{2\pi\mu c}\right)^{2}\frac{M'^{2} + N'^{2}}{M^{2} + N^{2}} + \frac{R_{\rho}L_{1}}{\pi\mu c}\frac{MM' + NN'}{M^{2} + N^{2}} + \frac{\rho L_{1}p(L_{0} - L_{1})}{\pi\mu c}\frac{MN' - M'N}{M^{2} + N^{2}} \right]^{\frac{1}{2}}.$$

Heaviside  $^{1}$  has given results from which this value of Z may readily be obtained.

By (14) and (15) R' and L' are expressed in terms of geometrical, electrical and magnetic constants of the coil and core, and of the four series M, N, M' and N', which are functions of the same constants and of the frequency. The formulas deduced are independent of the length of the coil, provided that the coil and the core are of the same length, and so long in comparison to the radius of the coil section that the magnetic field may be assumed to be uniform along any parallel to the axis without appreciable error.

#### Apparatus and Method.

The direct subjects of experimental observation were the effective resistance and inductance of a coil with different metallic cores and at various frequencies of the impressed electro-motive force. From these results the impedance under the same conditions was calculated.

The effective resistance and inductance were also calculated from (14) and (15), and from their values the theoretical impedance was calculated.

A tube was made of paper wound on a form in layers, the inside diameter being 1.905 and the outside diameter 2.54 centimeters. The paper was wound on a  $\frac{1}{4}$  inch bar, the layers being stuck together with shellac. Wooden end pieces were glued on, leaving a winding space 38.75 centimeters long. Three layers of number

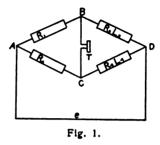
<sup>1</sup> See Electrical Papers, Vol. I., page 353.



29 double cotton covered wire were wound on, the layers having 625, 624 and 625 turns respectively, giving a density of winding of n = 1.874/38.75 = 48.361.

The resistance of the coil was carefully measured with a Wheatstone bridge and is R = 49 ohms =  $49 \times 10^9$  at 22° C. The in-

ductance was measured by Maxwell's bridge method, using an alternating current and telephone, as described by Max Wien,<sup>1</sup> and was found to be L = 7.2milli-henrys  $= 7.2 \times 10^6$ . The alternating current was supplied by a small rotary converter run as an inverted rotary from a storage battery, and supplying current at two or three volts. As a



standard of inductance for this and the later work a movable coil variable inductance, Ayrton and Perry form, made by the Leeds and Northrup Co. was used. This standard, which had a range from 4 to 40 milli-henrys, had been calibrated previously by Miss Agnes Childs, by comparing it with a coil wound on plaster whose inductance had been calculated from Maxwell's formula.

In measuring the resistance and inductance of the coil with the core inserted, the connection was as in Fig. 1.  $R_1$  and  $R_2$  are noninductive resistances, in the experiments the 100-ohm and 20-ohm coils of a box of coils were used.  $R_s L_s$  is the movable coil standard inductance, with non-inductive resistance added,  $R_4L_4$  is the coil under examination. In the work  $R_1$  and  $R_2$  were taken from a box of coils, the ratios of the coils of which had been adjusted with especial care by Professor Hooper of Tufts College. This was important because the ratio comes into the results instead of the actual value of either.  $R_s$  is the resistance of the standard inductance, 9.25 ohms, in series with as much as was needed to give a balance, taken from a Leeds box. When a harmonic difference of potential is maintained between the points A and D there will be silence in the telephone T if the resistances and inductances have the relations  $L_4/L_3 = R_4/R_3 = R_2/R_1 = .2$ , since  $R_2$  and  $R_1$  were kept at 20 ohms and 100 ohms respectively and the adjustment for balance made entirely in  $R_{s}$  and  $L_{s}$ .

<sup>1</sup>See Annalen der Physik und Chemie, Bd. 44, 1891, pp. 681-688.

The reaction of the core currents on the resistance and inductance of the coil varies with the frequency, see (1), accordingly there is no adjustment of resistances and inductances which will produce a balance and hence silence in the telephone unless the electro-motive force is harmonic. It was at first thought that this fact would make it impossible to use a telephone, as no means were available to produce a harmonic wave of electro-motive force of sufficient intensity and range of frequency for the work.

The first attempt therefore was to use a vibration galvanometer constructed on the principle of the one described by Max Wien,<sup>1</sup> with which he had secured good results.

With an instrument of this sort and for the purpose in mind the electro-motive force need not be even approximately harmonic for successful working, the one essential is that the fundamental period shall remain constant. The effect of the components of higher frequency than the one for which the instrument is adjusted is hardly noticeable. A tuning fork can be arranged to open and close the primary circuit of an induction coil with the required regularity, thus giving an alternating current in the secondary, but the frequency which can be obtained in this way is comparatively low, and its range is small, while the range that is obtainable requires a set of rated forks or else considerable labor in the rating of an adjustable fork at different speeds. On this account a great deal of work was done and much time was spent in trying to run an alternating current generator steadily enough to be used as the source of supply of the current. In the first place a 56 pole field magnet was mounted on the shaft of a direct current motor driven from a storage battery, an alternating current armature being supplied in proper relation to the field magnet. This attempt was not successful, as the speed varied between altogether too wide limits. Α small direct current motor was supplied with collector rings and connected as a rotary converter, to be run as an inverted rotary from a storage battery, the same in fact as was used in measuring the inductance of the coil. Several governors were tried, but none could be devised that would give the required steadiness of speed, and it was finally concluded that the measurements could not be

<sup>1</sup>See Annalen der Physik, Bd. 4, 1901, pp. 440-445.

made with the galvanometer at any but low frequencies. This plan was therefore dropped, as the core reactions increase rapidly with the frequency and hence measurements at high frequencies were especially desired. The writer has given <sup>1</sup> an account in an earlier paper of the results of certain experiments with the Wien vibration galvanometer.

The next attempt, and one that proved successful, was with a telephone. The first plan was to take the current used in the measurements from the secondary winding of an air core transformer. Capacity was to be inserted in series with the primary, so adjusted as to counterbalance the inductance in the primary and dynamo for the fundamental frequency, and thus make the overtones comparatively small in amplitude, obtaining an approximately harmonic current in the secondary and in the observing apparatus, as described by Pupin.<sup>2</sup>

As a source of primary current a motor-generator set in the electrical engineering laboratory of Tufts College was selected. The alternating current generator of this set was designed and partly built by the writer about ten years ago while a student in Tufts College. The set was intended for experimental purposes, and it, together with any other of his apparatus desired, was put at the disposal of the writer, for this work, by Professor Hooper.

The generator is of the Mordey disk type, with 24 pairs of poles and 48 armature coils. The armature is divided into twelve sections of four coils each, with connections brought out to a switchboard, and so arranged that the sections can be put into various combinations of series and multiple grouping. The shaft is rigidly clutched to the shaft of the driving motor of the set, a six pole, shunt wound, continuous current motor, run from a storage battery. The set will run steadily at any speed from 150 to 2,600 revolutions per minute, giving a range of frequency from 60 to 1,040 cycles per second.

The form of the electro-motive force wave is not exactly known, but it is not far from harmonic, enough however so that the telephone gave a distinct sound for any adjustment of the bridge arms with a core in the coil. Preliminary experiments were made with

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<sup>&</sup>lt;sup>1</sup> PHYSICAL REVIEW, Vol. XXIII., No. 6, December, 1906, p. 504.

<sup>\*</sup>American Journal of Science, Vol. 48, 1894, pp. 379-389 and 473-485.

the current from a 16 pole alternator run from a steam engine, and the attempt was made to balance with capacity the inductance of the primary of an air core transformer and the dynamo in series. In getting the circuit into electrical resonance a dynamometer was inserted in the primary and the capacity adjusted to give the maximum current, which was considered to be the point of resonance. With the condensers available it was in general possible to get only approximate resonance, and this was frequently annuled by the change in the inductance of the primary on closing the secondary. A few attempts were then made to take bridge measurements without any attempt to weed out the overtones of the current wave. It was found that with the shrill sound of the overtones always present in the telephone it was easy to fix a balance for the fundamental frequency, and this with great accuracy for frequencies of 250 cycles per second or over. With lower frequencies the possible accuracy of adjustment is a little less, and accordingly readings were taken at less intervals of frequency at low frequencies than at high, in order to get sufficient data for plotting smooth curves of resistance and inductance.

#### RESULTS.

On account of the varying permeability of iron it was decided to confine attention to non-magnetic cores, and copper, aluminum and brass were selected as giving a good range of resistivities. Cores of each metal were prepared, 38.75 centimeters long and 1.905 centimeters in diameter. The brass was cut from a stock bar in the laboratory shop and its resistivity measured. As a standard of resistance, a piece of soft drawn trolley wire was especially drawn by the American Steel and Wire Co., who also furnished its resistance. This was put in series with the brass, and a current passed through the two. A frame was prepared carrying two knife edges insulated from each other and 35 centimeters apart, which were laid on the bar. Two knife edges were prepared which could be put in contact with the trolley wire at a variable measured distance apart. Terminals from all four knife edges were brought to a Pohl's comdifference of potential between edges could be made the same in the two pairs, as shown by equal galvanometer deflection. Since the current in the brass bar was the same as that in the copper wire the resistances between the pairs of connected points was the same, and the resistivity of the brass could be obtained in terms of that of the copper. Four comparisons were made, the deflections being equalized in both directions for each of two current values. The four results agreed very well, giving as a mean the value of the resistivity of the brass as  $\rho_{b} = 7,850$ . The only galvanometer available was of the needle type, and although it was surrounded by a thick shield of iron filings, it was a good deal affected by the magnetic field from a nearby car line. In measuring the resistivity of the aluminum bar the maximum deflection that could be obtained was small on account of the low resistance of the bar and the drift due to the car line was serious. The value obtained is  $\rho_a = 3,035$ , which is liable to an error of a few per cent. due to the drift. On account of the cer-

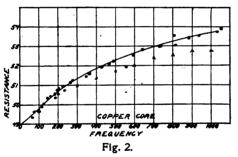
1	Copper.		Alumi	num.	Brass.		
	R'	Ľ	R'	L'	R'	L'	
0	49.00	7.20	49.00	7.20	49.00	7.20	
78	49.65	6.20	49.65	6.75	49.85	6.86	
100	49.65	6.46	49.25	6.80	49.95	7.00	
124	50.05	6.24	49.85	6.75	49.45	7.14	
145	50.35	6.17	50.35	6.48	49.85	7.06	
160	50.45	6.02	50.35	6.45	49.75	7.04	
188	50.35	6.17	50.35	6.48	49.85	7.06	
196	50.75	5.68	50.75	6.28	49.95	6.97	
205	50.85	5.64	50.85	6.30	50.35	6.94	
225	50.95	5.46	51.05	6.10	50.35	6.90	
234	50.75	5.47	50.85	6.07	50.25	6.90	
277	51.25	5.30	51.55	5.85	50.95	6.76	
348	51.45	5.10	51.95	5.56	51.75	6.57	
429	51.95	4.96	52.55	5.35	52.65	6.35	
<b>49</b> 0	52.25	4.92	53.05	5.24	53.45	6.17	
556	51.95	4.84	52.85	5.12	53.55	6.05	
640	52.85	4.78	53.65	5.04	54.75	5.84	
732	53.05	4.74	54.05	4.95	55.45	5.69	
806	53.55	4.68	54.35	4.89	55.95	5.55	
811	53.05	4.69	54.05	4.84	55.65	5.56	
938	53.55	4.64	54.65	4.80	56.65	5.40	
1,032	53.75	4.59	54.95	4.78	57.25	5.35	

TABLE I.

	Cop	Copper.		Aluminum.		
,	R'	L'	R'	L'	R'	L'
100	49.71	6.46	49.52	6.88	49.23	7.15
200	50.57	5.69	50.48	6.29	49.85	7.00
300	51.00	5.31	51.30	5.83	50.73	6.79
400	51.38	5.11	51.90	5.35	51.71	6.55
500	51.71	4.98	52.35	5.33	52.68	6.33
600	52.01	4.89	52.76	5.19	53.58	6.12
700	52.41	4.82	53.12	5.09	54.34	5.94
800	52.55	4.76	53.45	5.02	55.11	5.80
900	52.74	4.71	53.76	4.95	55.75	5.67
1,000	52.78	4.67	53.94	4.90	56.59	5.60

INDLE II.	Τa	BLE	II.
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tainty of a still greater error in the measurement of the resistivity of the copper, because its lower value would cause a still smaller gal-



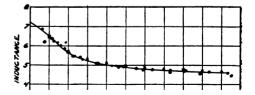
vanometer deflection, Matthiessen's value of 1,590 at 0° C., and a temperature coefficient of .4 per cent. were used, and 3 per cent. added for impurities, giving a value  $\rho_c = 1,782$  at 22° C.

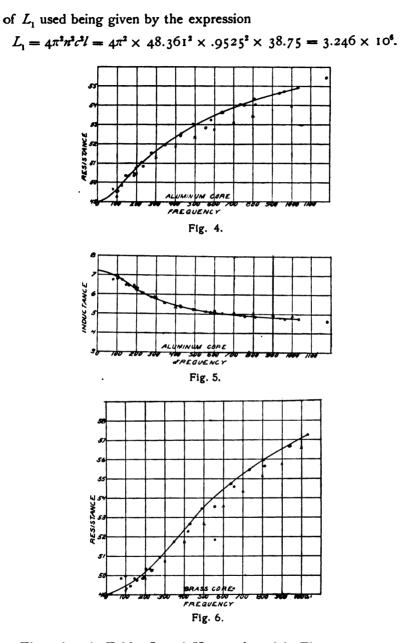
In taking the final observations with coil and core an incandescent lamp was

inserted in the dynamo circuit, to make sure that no injuriously large current should flow through the box of coils.

The observed resistances and inductances of the coil with the different cores and at different frequencies are given in Table I R' being in ohms

350

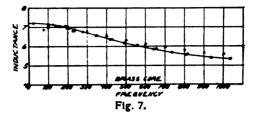




The values in Tables I. and II. are plotted in Figs. 2, 3, 4, 5, 6 and 7. In these curves the observed points are shown as dots sur-



rounded by circles, a full line being drawn, while the points calculated from (14) and (15) are shown as crosses.



The impedance of the coil with the three cores was calculated for various frequencies up to 1,000, from the curves of observed values of R' and L' by steps of 50, and from the values of R' and L' from (14) and (15) by steps of 100. These results are given in Table III.

These results are plotted in Figs. 8, 9 and 10 using the same convention as to circles, crosses and kinds of lines as in Figs. 2 to 7.

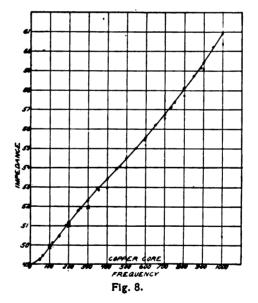


Table IV. gives the difference in the increase of impedance with frequency, which is the real test of the accuracy of the work, as obtained from formulas (14) and (15), and from the observations, marked + or - according as the latter is larger or smaller than the

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former, and the percentage that this difference is of the value as obtained from the formulas.

£	Сор	per.	Aluminum.		Brass.		
	Formulas.	Observed.	Formulas.	Observed.	Formulas.	Observed	
0		49.00	I	49.00		49.00	
50	!	49.25		49.14		49.05	
100	49.88	49.94	49.71	49.70	49.43	49.40	
150		50.48		50.58		49.97	
200	51.07	51.19	51.10	51.42	50.62	50.76	
250		51.80		52.13		51.62	
300	51.98	52.32	52.46	52.78	52.32	52.62	
350		<b>52.92</b>		53.30		53.61	
400	52.96	53.40	53.73	54.08	54.27	54.68	
450		<b>53.96</b>		54.73		55.76	
500	54.02	54.50	54.97	55.39	56.31	56.75	
550		55.02		56.13		57.74	
600	55.18	55.56	56.27	56.72	58.34	58.80	
650		56.22		57.42		59.73	
700	56.56	56.75	57.65	58.08	60.29	60.65	
750 ·		57.38		58.81		61.68	
800	57.74	58.11	59.11	59.46	62.35	62.47	
850		58.72		60.19		63.40	
900	59.10	59.42	60.61	60.98	64.31	64.36	
950		60.22		61.73		65.21	
1,000	60.39	60.95	62.11	62.51	66.64	66.14	

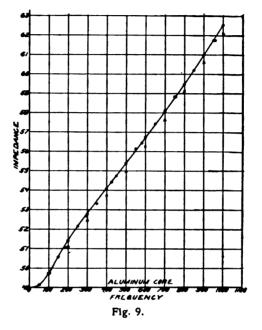
TABLE III.

	Copper.		Aluminum.		Brass.		
1	Diff.	Per Cent. Diff.	Diff.	Per Cent. Diff.	Diff.	Per Cent. Diff.	
100	+.06	6.82	01	1.41	03	6.98	
200	+.12	5.80	+.32	15.24	+.14	8.64	
300	+.34	11.41	+.32	9.25	+.30	9.04	
400	+.44	11.11	+.35	7.40	+.41	7.78	
500	+.48	9.56	+.42	7.04	+.44	6.02	
600	+.38	6.15	+.45	6.19	+.46	4.93	
700	+.19	2.51	+.43	4.97	+.36	3.19	
800	+.37	4.23	+.35	3.46	+.12	.90	
900	+.32	3.17	+.37	3.19	+ .05	.33	
1,000	+.56	4.92	+.40	3.05	50	2.83	
		Mean 6.57%		Mean 6.12%	1	Mean 5.06%	

•

TABLE IV.

An examination of the tables and curves shows that in nearly every case the observed resistance is more and the observed inductance is less than the results calculated from (14) and (15). In general, however, the two sets of values lie on curves of the same shape, and near enough together so that we may consider the



formulas deduced to be verified by experiment. The differences are undoubtedly due, partly to errors of observation, and to greater degree to using in the calculations incorrect values of the resistivity and the inductance of the core. In the impedance curves the agreement is much better, the differences in resistance and inductance tending to compensate for each other.

The curves of Figs. 2 to 7 show that both resistance and inductance tend to a limiting value as the frequency increases, the frequency at which the limiting value of either is reached increasing with the resistivity of the core. The final limits of resistance and inductance seem to increase with the resistivity of the core also, as would be expected from (I).

For comparison the impedance of the coil with no core and the observed impedances with the different cores are given in Table V.



ſ	Copper.	Aluminum.	Brass.	No Core
0	49.00	49.00	49.00	49.00
100	49.88	49.71	49.43	49.21
200	51.07	51.10	50.62	49.83
300	51.98	52.46	52.32	50.84
400	52.96	53.73	54.27	52.23
500	54.02	54.97	56.31 ·	53.97
600	55.18	56.27	58.34	56.02
700	56.56	57.65	60.29	58.34
800	57.74	59.11	62.35	60.92
900	59.10	60.61	64.31	63.71
1,000	60.39	62.11	66.64	66.69

TABLE V.

These results are plotted in Fig. 11. From them it is seen that at low frequencies the impedance is increased by the insertion of any

one of the cores, but as the frequency increases the decrease in inductance when multiplied by  $2\pi$  times the frequency is more than enough to counterbalance the increase in resistance, and the impedance is decreased by the insertion of a core. Thus the curve of impedance with no core crosses successively the curves of impedance with the different cores, and at a frequency increasing with the inin resistance crease change and decrease in inductance change due to the core, that is, with the resistivity of the core.

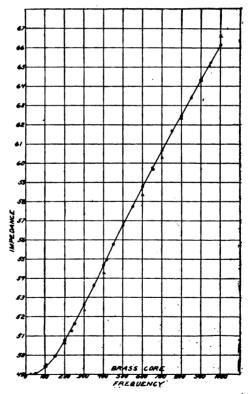
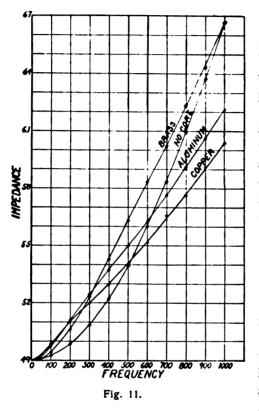


Fig. 10.

The results obtained from observation and those obtained by computation from formulas (14) and (15) agree in the shape of the curves in general, there is, however, a considerable difference, as shown by Table IV., the difference in increase of impedance being



from .33 per cent. to 15.24 per cent., with a mean of 5.92 per cent. While the similarity in the shapes of the curves proves definitely the correctness of the theory as developed, the fact that the computed resistance is too great and the computed inductance too small, in nearly every case, indicates that a systematic error was made in the computations.

The computation of resistance and inductance involves two constants for each core, namely, the resistivity of the core and the inductance  $L_1$ , the latter being the same for all cores, and it is probably due to using incor-

rect values of these constants in the computations that the curves do not agree better. The determination of all of them was subject to error with the means available. Mr. Gordon Fulcher, assistant to Professor A. G. Webster, has at the suggestion of the latter determined by a process of trial values for  $L_1$  and the resistivities of the cores which when used in formulas (14) and (15) give results which agree closely with those observed, and those computed from the observations. These values found by Mr. Fulcher are  $L_1 =$  $3.60 \times 10^6$ , and resistivities of 2,100, 3,400 and 7,500 for copper, aluminum and brass respectively. When these values are used in

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formulas (14) and (15) they give the following results, resistance and inductance directly and impedance by calculation.

Copper.			Aluminum.				Brass.				
	R'	L'	Z	ſ	R'	L'	Z	ſ	R'	Ľ	Z
66	49.34	6.87	49.46	107	49.56	6.87	49.77	26	49.02	7.195	49.03
117	49.91	6.39	50.13	190	50.48	6.39	51.05	105	49.29	7.145	49.51
183	50.56	5.88	51.01	297	51.53	5.88	52.68	236	50.23	6.87	51.25
264	51.15	5.40	51.93	427	52.48	5.40	54.44	419	52.27	6.39	54.91
359	51.64	5.09	52.86	581	53.28	5.09	56.43	654	54.58	5.88	59.6
469	52.10	4.89	54.06	759	54.01	4.89	58.83	<b>94</b> 2	56.67	5.40	65.0
594	52.55	4.74	55.45	961	54.74	4.74	61.77				
733	53.00	4.62	57.11	1,186	55.48	4.62	65.29				
889	53.47	4.53	59.15								
1,055	53.94	4.45	61.48								

TABLE VI.

These results are plotted in Figs. 2 to 10, being shown as heavy dots, and show an excellent agreement with the results as obtained from observation.

In conclusion there remains only to express my thanks to all who have assisted in making this work possible; to Mr. Southerland of the American Steel and Wire Co. for having drawn for me the soft copper used, to Mr. Fulcher for his tedious work of computation, to Professor Hooper, of Tufts College, for placing his equipment at my disposal, to Clark University for the opportunity to work in the laboratory, and especially to Professor A. G. Webster for his continual kindness, both in suggesting the work and in assisting while it was in progress.

CLARK UNIVERSITY, WORCESTER, MASS., June, 1903.

### INDUCTION COILS.

#### BY BENJ. F. BAILEY.

M<sup>Y</sup> object in this investigation was first and principally to establish the conditions of maximum efficiency in primary coils, and to deduce a method whereby the efficiency of such coils could be predetermined from their electrical design; secondly to verify experimentally this theory; and thirdly to study the ordinary induction coil with secondary current from both theoretical and experimental standpoints. The efficiency of the secondary coil was also investigated and determined experimentally in the case of one coil.

By an induction coil I mean an apparatus in which magnetic energy is stored, to be used later in some different form from that in which it was supplied. Ordinarily, it is also to be understood that the charging of the coil is to be accomplished from a constant potential source, and usually, the intention is to utilize the stored energy at a higher potential and at a greater wattage than that at which it was supplied. Such coils are made in a great variety of The simplest is a plain coil of one or more turns of a nonforms. magnetic conductor, and an arrangement for making and breaking the circuit. Such an apparatus will not store much energy per unit of weight and consequently can be used economically only when it is charged and discharged a great many times per second. An example of this is the Tesla high frequency coil. For ordinary purposes the introduction of an iron core greatly increases the capacity of the coil. The voltage obtainable from such a coil is still rather

## PRIMARY OR SINGLE CIRCUIT COILS.

The primary coil, while a relatively unimportant device, is used in the ignition of almost all stationary gas engines and with many boat and automobile engines. Moreover, the theory of these coils as developed here will be used directly in considering the case of the double circuit or ordinary induction coil. This, together with the fact that so far as I know, nothing has been written regarding the theory of the primary coil, is the reason for my taking it up here. The first point to be considered is the efficiency of such coils.

## EFFICIENCY OF PRIMARY COIL.

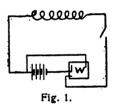
By the efficiency of any piece of electrical apparatus we mean the ratio of the useful work obtained from it to the total work put into it. In obtaining this for any piece of apparatus two methods are in general available. The most obvious one is to measure these quantities directly. The case of the simple primary circuit is shown in Fig. I. To apply this method we might use a

wattmeter as indicated to measure the input. Theoretically, the output might be measured by transferring the connection a, from the terminal of the battery to the other side of the break at b. Practically, this would not work well for several reasons. For one thing the high voltage at

the break would be liable to puncture the insulation of the wattmeter. Moreover, the amount of power required to operate the wattmeter is large compared to the power of the spark; or stated differently, a large part of the current would shunt off through the wattmeter instead of passing across the gap. This would obviously affect the intensity of the spark, making it much less than it should be. Also since the current and E.M.F. are far out of phase, the self-induction of the wattmeter coils would cause the results to be in error to a considerable extent.

Another method of accomplishing the same object would be to measure the heat produced by the spark by means of a small calorimeter. This method is difficult to apply and is not very accurate.

The method here deduced is in principle the same as that used to predetermine the efficiency of all large generators, transformers, etc.



It is based upon the principle of the conservation of energy, i. e., all the energy that goes into the coil must appear in some form or other. Part appears as the energy of the spark and the rest is wasted in various losses. Stated mathematically we have

Eff. = 
$$\frac{\text{output}}{\text{input}}$$
 =  $\frac{\text{output}}{\text{output} + \text{losses}}$ 

This method is comparatively easy to apply to the case of a dynamo or transformer. With a spark coil it is more difficult, as the calculations are more involved owing to the shape of the waves used. It should be remarked that while the method appears indirect at first, it is in reality preferable to the direct method, both on the score of accuracy, and even more because it shows the magnitude of the various losses, and thus indicates how the design of the coil may be modified so as to improve it.

COIL WITHOUT IRON CORE. INSTANTANEOUS BREAK.

We will first take up the case of a coil without an iron core. This is the simplest case as there are no iron losses to consider. In a circuit like that of Fig. 1 in which the total resistance of the circuit is R and the inductance is L, the differential equation is:

$$E = Ri + L\frac{di}{dt}$$

and

$$i = I(1 - e^{-Rt/L}).$$

The magnetic energy stored in the coil at any instant is  $\frac{1}{2}Li^2$ . If the circuit is broken instantaneously, all of this energy (with the possible exception of a small loss due to eddy currents in the copper) appears as the energy of the spark. This will be practically all heat energy, but a small proportion may be radiated as electromagnetic waves. It is here assumed that all the energy of the spark is used, and the output is consequently  $\frac{1}{2}Li^2$ .

The input will be the output plus the losses. The latter here consist merely of the ohmic loss in the winding, during the process of building up the magnetism. To get this we must find

$$\int_0^{T} Ri^2 dt.$$

R is a constant and substituting for i we get

$$R\int_{0}^{T} i^{2}dt = R\int_{0}^{T} I^{2} \left(1 - \varepsilon^{-\frac{Rt}{L}}\right)^{2} dt$$
$$= RI^{2} \int_{0}^{T} \left(1 - 2\varepsilon^{-\frac{Rt}{L}} + \varepsilon^{-\frac{2Rt}{L}}\right) dt.$$

Integrating this we get

$$RI^{2}\left[T+\frac{L}{2R}\left(1-\varepsilon^{-\frac{2RT}{L}}\right)-\frac{2L}{R}\left(1-\varepsilon^{-\frac{RT}{L}}\right)\right]=Om.$$

The total input is

$$\frac{1}{2}Li^{2} + Om = \frac{1}{2}Li^{2} + RI^{2}T + \frac{1}{2}LI^{2}(1 - e^{-2RT/L}) - 2LIi$$

which readily reduces to  $RI^{2}T - LIi$ . The efficiency then becomes

$$\eta = \frac{\frac{1}{2}Li^2}{RI^2T - LIi}.$$

This gives the efficiency in terms of L, i, R, I, and T. It is obvious that these quantities are interconnected, and by eliminating we should arrive at a simpler form. To eliminate T take logarithms of both sides of

$$\frac{I-i}{I} = \varepsilon^{-\frac{RT}{L}}$$

and get

$$T = \frac{L}{R} \log \frac{I}{I - i}.$$

Substituting this in the above we obtain

$$\eta = \frac{\frac{1}{2}i^2}{I^2 \log \frac{I}{I-i} - Ii}.$$

This gives us at once the very peculiar results that the efficiency is independent of both the resistance and the inductance and depends only on the value of the current at the instant of break and upon its steady value. This may be made clearer and some new laws brought out by a further change.

To do this substitute

$$\log \frac{I}{I-i} = \left(\frac{i}{I}\right) + \frac{1}{2} \left(\frac{i}{I}\right)^2 + \frac{1}{3} \left(\frac{i}{I}\right)^3 + \cdots,$$

simplify and get

$$\eta = \frac{\frac{1}{2} {\binom{i}{f}}^{*}}{\frac{1}{2} {\binom{i}{f}}^{*} + \frac{1}{3} {\binom{i}{f}}^{*} + \frac{1}{4} {\binom{i}{f}}^{*} + \cdots}$$

Or if we designate the ratio i/I by a we obtain

$$\eta = \frac{\frac{1}{2}\alpha^{3}}{\frac{1}{2}\alpha^{3} + \frac{1}{8}\alpha^{3} + \frac{1}{4}\alpha^{4} + \cdots}.$$

From this very simple form we can at once deduce several important conclusions.

I. The efficiency is entirely independent of the ohmic resistance of the coil, for a given ratio of i/I.

II. The efficiency is entirely independent of the inductance of the coil.

III. The efficiency is a function of the ratio of the current at break, to the current which would flow if the contact were very long.

IV. The efficiency is a maximum and equal to 100 per cent. for i = 0.

V. The efficiency is a maximum and equal to 100 per cent. for  $I = \infty$ .

We may write the expression for the efficiency as follows :

$$\eta = \frac{\frac{1}{2} \left(\frac{iR}{E}\right)^2}{\frac{1}{2} \left(\frac{iR}{E}\right)^2 + \frac{1}{3} \left(\frac{iR}{E}\right)^2 + \frac{1}{4} \left(\frac{iR}{E}\right)^4 + \cdots}$$

We then conclude in addition to the above

VI. With given values of R and *i* the efficiency is a maximum and equals 100 per cent. for  $E = \infty$ .

VII. With fixed values of E, i and L the efficiency is a maximum and equals 100 per cent. for R = 0.

This latter condition is the one present in practice. E is fixed, at least to a certain extent, by the cost and the difficulty of carrying many cells in vehicles or boats. L being also fixed, *i* must not be less than a certain value or the resultant spark will not be sufficiently intense to ignite the charge. Under these conditions Rshould be as small as possible with the given inductance.

No. 5.]

INDUCTION COILS.

The above facts can also all be proved by direct differentiation of the formula

$$\eta = \frac{\frac{1}{2}i^2}{I^2 \log \frac{I}{I-i} - iI}.$$

So far, we have neglected entirely the influence of the time of break. It is evident that during this time an additional amount of energy is drawn from the battery. Part of this appears as heat in the spark, and the rest is wasted in  $I^3R$  loss in the resistance of the coil.

To calculate the magnitude of this effect, it is necessary to know something about the shape of the current curve during the time that the circuit is being opened. To deduce mathematically the shape of this curve would be difficult if not impossible. It will be seen, however, from the accompanying curves that it is practically a straight line. Assuming this to be the case, the current may be expressed by i = K(T - t) in which T is the time that elapses from the beginning of opening of the circuit until the resistance becomes infinite and t is the time. Since at t = 0,  $i = i_b$ ,  $K = i_b/T$  or  $i = i_b/T(T - t)$ .

We may now readily modify our expression for efficiency so as to include this factor. The formula

$$\eta = \frac{\frac{1}{2} \left(\frac{i}{\overline{I}}\right)^2}{\frac{1}{2} \left(\frac{i}{\overline{I}}\right)^2 + \frac{1}{3} \left(\frac{i}{\overline{I}}\right)^3 + \frac{1}{4} \left(\frac{i}{\overline{I}}\right)^4 + \cdots}$$

may be written

$$\eta = \frac{\frac{1}{2}Li^2}{\frac{1}{2}Li^2 + LI^2 \left[\frac{1}{3}\left(\frac{i}{I}\right) + \frac{1}{4}\left(\frac{i}{I}\right)^4 + \cdots\right]}.$$

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#### EFFECT OF TIME OF BREAK.

To find the influence of the time of break upon the efficiency we differentiate with respect to T and place the result equal to zero. For this purpose we may regard everything except T and  $\eta$  as constant and write

$$\eta = \frac{K_1 + K_2 T}{K_3 + K_4 T}$$

Then

$$\frac{d\eta}{dT} = \frac{K_2 K_3 - K_1 K_4}{(K_3 + K_4 T)^3}.$$

This is satisfied for  $T = \infty$  and in this case we have

$$\eta = \frac{K_2}{K_4} = \frac{\frac{1}{2}Ei - \frac{1}{3}Ri^3}{\frac{1}{2}Ei} = 1 - \frac{2}{3}a.$$

The efficiency with T = 0 was

$$\gamma = \frac{\frac{1}{2}a^2}{\frac{1}{4}a^2 + \frac{1}{3}a^3 + \cdots} = 1 - \frac{2}{3}a - \frac{1}{18}a^2 - \frac{2}{135}a^3 - \frac{47}{620}a^4 \cdots$$

The first two terms of these expressions are the same, and they differ only by small multiples of  $a^2$ ,  $a^3$ , ..., etc. Hence, when the ratio a = i/I is small, the efficiency is very little affected by the speed of break. In any case however it becomes somewhat greater as the time of break becomes larger.

THE SPARK COIL WITH IRON CORE.

The coil without iron, while it may have high efficiency as has been shown, is probably impracticable for ordinary purposes. Almost the only use to which primary coils are put, is the ignition of gas engines, for gas lighters, and similar uses. Experience shows that for such work an output of about  $60 \times 10^{-4}$  joules is required. If *i* be taken as 1 ampere, which is about as much as we would care to use from the ordinary primary battery, we have, assuming 100 per cent. efficiency,  $\frac{1}{2}Li^2 = 60 \times 10^{-4}$  or L = 1.0120/1 = .012henry. A coil without an iron core, to have this inductance, would necessarily be of very large size. This is true since it would have to be wound with coarse wire to keep the ratio i/Ismall when used with a moderate voltage.

The introduction of an iron core gives us three additional losses

INDUCTION COILS.

to compute. These are the hysteresis loss, eddy current losses at make and at break. We shall designate these respectively by H,  $E_{a}$  and  $E_{b}$ . The expression for efficiency then becomes

$$\eta = \frac{\frac{1}{2}Li^2 - E_b + I_b}{\frac{1}{2}Li^2 + E_m + O_m + H + O_b + I_b},$$

we have now to find expressions for H,  $E_m$  and  $E_b$ 

The hysteresis loss is best found by direct experiment. In the coil here considered three methods have been employed. One is to use a wattmeter and alternating currents, the other consists in obtaining the hysteresis curve or loop for the coil in question and from its area, as from an indicator card, obtaining the actual loss in one cycle. A third method is to compute the loss from the average values obtained from similar samples of iron and used by dynamo designers and others to predetermine hysteresis loss. The three methods give very concordant results. It is well known that this loss for each cycle varies as the 1.6 power of the flux density. The flux density for small values is proportional to the current, consequently we may write  $H = \text{constant} \times i^{1.6}$ . In the coil considered the constant is equal to  $4.69 \times 10^{-4}$  or  $H = 4.69 \times 10^{-4} i^{1.6}$ .

The loss due to eddy currents at the make has next to be determined. As the magnetic flux surges back and forth through the wire, currents, first in one direction, then in the other, will be generated and will flow in circles, through the wire. This current wastes power in heat, and, though the amount is small it is not negligible.

Consider a ring of radius r and thickness dr. If  $\varphi$  is the flux through this ring, the E.M.F. induced in it is  $e = d\varphi/dt$ . But we may write  $\varphi = Kai$ , where K is a constant depending upon the coil used and a is the area of the ring. Then

$$e = Ka\frac{di}{dt} = \pi r^2 K\frac{di}{dt}$$

But

$$i = I(1 - e^{-Rt/L}),$$

 $\frac{di}{dt} = I \frac{R}{L} \varepsilon^{-\frac{Rt}{L}}.$ 

and

Substituting and dividing by 10<sup>-8</sup> to reduce to volts, we get



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$$e = 10^{-8} K \pi r^2 I \frac{R}{L} \varepsilon^{-\frac{Rt}{L}}$$

The resistance of the cylinder of which this ring is an element and of a length equal to the length of the coil, say l is equal to

Constant  $\times \frac{\text{length}}{\text{cross-section}} = \frac{K_1 2\pi r}{edr}.$ 

The power loss at any instant is

$$\frac{e^2 dr}{r} = \frac{K^2 \pi r^3 I^2 R^2 \varepsilon^{-2Rt/L \cdot l}}{10^{16} \times 2K_1 L^2} dr.$$

There are only two variables in the equation, t and r, and to find the rate of loss of energy in one wire of the core we must integrate with respect to r from 0 to D/2, where D is the diameter of the wire. Doing this, we get

$$w = \frac{K^2 \pi I^2 R^2 \epsilon^{-2Rt/L^2}}{10^{16} \times 2K_1 L^2} \int_0^{P/2} r^3 dr = \frac{K^2 \pi I^2 R^2}{10^{16} \times 128 L^2 K_1} \epsilon^{-\frac{2Rt}{L}} D^4.$$

To get the loss of energy in one cycle we must multiply this by dt and integrate again from 0 to  $T_m$ , where  $T_m$  is the time elapsing from the make to the break. This gives us

$$j = \frac{K^2 \pi I^2 R^2 / D^4}{10^{16} \times 128 K_1 L^2} \int_0^{T_m} \varepsilon^{-\frac{2Rt}{L}} dt = \frac{K^2 \pi I^2 R / D^4}{10^{16} \times 256 L K_1} (\varepsilon^{-\frac{2RT_m}{L}} - 1).$$

which may be readily simplified to

$$\frac{1.36K^2R/D^4}{10^{13}L}i(2I-i).$$

We can easily show that

$$K=\frac{10^{8}L}{NA},$$

where N is the number of turns of wire in the coil and A is the net area in square centimeters of the core. Then we have finally,

This is true for any coil, and if the value of L, R, l, D, W, N and A in any particular case be inserted it reduces to the form constant  $\times i(2I-i)$ . In the case of the coil here considered, it becomes  $7 \times 10^6 i(2I-i)$ .

To find the losses at the break we must know something about the way in which the current falls off during this time. Assuming as before that the current during break follows a straight line law we may take for our expression for the current  $i = -K_s t$ , taking a new origin for the time, for the sake of simplicity.

To get the eddy current loss at break we proceed as before, merely using our new value for i. Thus

$$e = \frac{d\theta}{dt}; \quad \theta = -Kai = -KaK_st;$$

then  $e = -KK_s a = -\pi r^2 KK_s$ . Taking r as before,

$$dw = \frac{e^2}{r} = \frac{\pi r^3 K^3 K_3^{3/2}}{2K_1} dr.$$

Then rate of loss of energy per wire per cycle equals

$$W = \frac{\pi K^2 K_3^2 l}{2K_1} \int_0^{D/2} r^3 dr = \frac{\pi K^2 K_3^2 l D_1^4}{128K_1},$$

and the energy loss in joules per cycle for the whole core of W wires, if  $T_b$  be the time of break, is

$$E_{b} = \int_{0}^{T_{b}} W dt = \frac{\pi K^{3} K_{3}^{2} / T_{b} D_{1}^{4} W}{128 K_{1}}.$$

If i is the value of the current at the instant of break, then

$$i = -K_s T_b$$
 or  $K_s = -\frac{i}{T_b}$  and  $K = \frac{L}{N\bar{A}}$ .

Substituting also for  $K_1$  its value for iron of  $9 \times 10^{-6}$  we get

$$E_{b} = \frac{\pi L^{2} i^{2} l T_{b} D^{4} W}{128 N^{2} A^{2} T_{b}^{2} \times 9 \times 10^{-6}} = \frac{\pi L^{2} l D^{4} 10^{3}}{1.152 N^{2} A^{2}} \times \frac{i^{2}}{T_{b}} \times W.$$

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The loss of energy in the coil during the break is next to be obtained. As before,  $i = -K_s t$ . The loss of energy equals

$$\int_{0}^{T_{b}} i^{4}Rdt = K_{3}^{4}R \int_{0}^{T_{b}} t^{2}dt = \frac{1}{8}K_{3}^{4}RT_{b}^{3}.$$

If, as before, i = current at time of break, then  $i = -K_s T_b$ and loss in joules per cycle =  $O_b = \frac{1}{8}Ri^2T_b$ . In the coil here considered R = 0.725 ohm, and we get  $O_b = 0.242i^2T_b$ .

We have to obtain now only the added energy furnished by the battery during the break. Since we have assumed that the current varies uniformly from a value i to zero during this time, the average power is evidently  $\frac{1}{2}Ei$ . Then the energy added equals

$$I_{b} = \frac{1}{2} E i T_{b}.$$

This gives us all the factors needed for the expression for efficiency. As before

$$\eta = \frac{\frac{1}{2}Li^2 + I_b - E_b - O_b}{\frac{1}{2}Li^2 + I_b + H + E_a + O_a}$$

Substituting the values we have just found for these factors, we obtain a general expression for the efficiency of any primary coil. Substituting the values of L, R, l, D, N, A,  $K_4$  and W for the coil under consideration the formula will be greatly simplified. In the case of the coil here considered it becomes

$$\eta = \frac{0.02i^2 + \frac{1}{2}EiT_b - 0.242i^2T_b - 7.85 \times 10^{-7}\frac{i^3}{T_b}}{0.02i^2 + \frac{1}{2}EiT_b + 4.69 \times 10^{-4}i^{1.6} + 7 \times 10^{-6}i(2I - i)} + 0.04I^2 \left[\frac{1}{3}\left(\frac{i}{I}\right)^3 + \frac{1}{4}\left(\frac{i}{I}\right)^4 + \cdots\right].$$

To apply this we must know the time of make and break. The former is most readily found by turning the engine over slowly by hand and observing the angle within which contact is made. Knowing the number of revolutions per minute we can easily compute the time of contact. The time of break cannot be obtained in any simple way. It will usually be about one one-thousandth of a second, however, and any small error in estimating it will have but very little influence upon the result. In the case of one engine it

was found that the time of contact was one one-hundredth of a second. Knowing this and the E.M.F. of the battery used, which was in this instance 2.52 volts, we can calculate the value of i.

Substituting in  $i = I(1 - e^{-Rt/L})$  we get

$$i = \frac{2.52}{0.725} \left( 1 - \varepsilon \frac{-0.725 \times \frac{1}{100}}{.04} \right) = 0.584$$
 ampere

and

$$I = \frac{E}{R} = \frac{2.52}{0.725} = 3.5$$
 amperes.

Substituting these values in the formula we find the efficiency equal to 82.5 per cent. That is, of the actual energy put into the coil 82.5 per cent. appears in the heat of the spark, the other 17.5 per cent. being wasted in the various losses.

It is of some interest to compare these losses with one another and with the input. They are given in the following table:

Magnetic energy,	$\frac{1}{2}Li^2 = 68.4 \times 10^{-4}$ joules
Energy added during break,	$Ib = 7.35 \times 10^{-4}$ joules
Ohmic loss at make,	$Om = 8.80  imes 10^{-4}$ joules
Ohmic loss at break,	$Ob = 0.83 \times 10^{-4}$ joules
Eddy current loss at make,	$Em = 0.25 \times 10^{-4}$ joules
Eddy current loss at break,	$Eb = 2.68 \times 10^{-4}$ joules
Hysteresis loss,	$H = 2.03 \times 10^{-4}$ joules

Of these the largest is the ohmic loss at the make. This can be reduced by using a battery of higher E.M.F. and a correspondingly short make. This is readily seen to be true, since this loss is dependent upon the ratio of i/I, and increasing the E.M.F. increases I in the same proportion. The ohmic loss at the break is small in any case, and can be still further reduced by shortening the time of break.

In the eddy current losses we have an opposite set of conditions, since each is increased by a decrease of the time of make or break. Hence the conditions for best efficiency here are the exact opposite to those applicable to the ohmic losses. Fortunately, the eddy current loss can be reduced to any desired extent by using finer wires in the core. For a given cross-section of core the loss is in proportion to the square of the diameter. It will be noticed that the loss is, of course, much larger at the break than at the make. Hence it has an especially bad effect, as it takes away materially from the energy of the spark. Indeed, a short calculation shows that if the break takes place in about thirty-five millionths of a second all the energy would be wasted in the eddy currents.

The magnitude of the hysteresis loss is independent of the time of the make or break, and depends only on the value of the current used and the quality of the iron. To reduce it as far as possible, iron having the smallest hysteresis loss possible should be used.

In any piece of apparatus the efficiency curve is of importance; that is, it is important to see whether the efficiency keeps up well through a wide range of load. I have computed the efficiency for various values of the current *i*, that is, the current at which the break takes place, the results being given in Table I. The values of *i* correspond to an intensity of spark from 0 to 0.04 joule. The actual value of *i* used, it will be remembered, is 0.584 ampere, corresponding to 0.0075 joule per spark. At i = I = 2.5 amperes the efficiency would drop to zero.

	Table I.
Efficiency fo	or Different Values of i.
i	Efficency.
0	77 per cent.
0.1	83 ''
0.2	85 ''
0.4	83 ''
1.0	81 "

The fact that the efficiency stays above 80 per cent. up to about five times the spark intensity used shows that the coil is capable of delivering a spark five times as strong as actually used and still preserve a good efficiency, or, conversely, a very much smaller coil would be capable of doing the work required. At the same time a slightly greater efficiency could be obtained by an even larger coil. However, the gain would be slight and it would seem better to reduce considerably the size of the coils usually used.

To summarize — for the highest efficiency the battery should have a rather high E.M.F. and the contact should be short, so that the

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smallest possible hysteretic coefficient. For the sake of first cost, the coil could be much smaller than those usually used.

EXPERIMENTAL WORK WITH THE PRIMARY INDUCTION COIL.

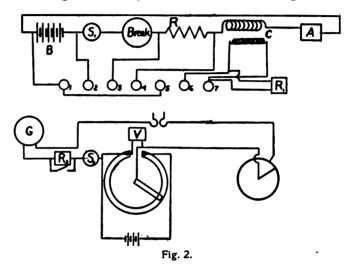
The preceding theory is, it is believed entirely new, and it seemed desirable to confirm it by direct experimental proof. The method adopted is equally applicable to the ordinary induction coil with a secondary winding, and was used in obtaining various results in connection with such coils.

The first point taken up was an experimental determination of the efficiency of a primary coil. The method adopted was to obtain by means of an instantaneous contact maker, a series of points on the curves of current and E.M.F. of the coil. The summation of the products of E.M.F. and current will give us the energy input and output and consequently the efficiency, and in addition we learn the way the current rises, how it falls off, the inductive rise of pressure at the break, both across the gap and over the coil, the potential difference of the battery, etc. These are gotten directly and having them we may easily compute the values for the curves of power during make and break, the resistance or conductivity of the gap during break, and the internal resistance of the battery.

Some difficulty in obtaining points especially during the break was anticipated. Looking at the sparks, they appear to differ considerably in length, quality, etc., and hence it was feared that it would be impossible to secure consistent results. Some trouble was encountered from this source, but by keeping the contacts clean, this was reduced to a minimum.

The use of the oscillograph to obtain these curves has been suggested, and for merely qualitative results it could undoubtedly be employed to very great advantage. For accurate work, however, it could hardly be used with spark coils. For one thing it would take a relatively large amount of energy from the circuit, especially during the break. For example, the oscillograph manufactured by the General Electric Company requires 0.3 ampere for its operation. At the break the voltage rises to from 50 to 100 volts, and consequently from 15 to 30 watts would be expended in the instrument. Since the maximum wattage of the spark rarely exceeds twice these figures, it is evident that this method is out of the question for the determination of the efficiency. This objection does not apply to the oscillograph when used on circuits carrying considerable amounts of power.

The arrangement of the apparatus used is shown in Fig. 2. The main circuit is shown in the upper part of the figure and comprises from left to right a battery B a switch S, a rotating break Br, a



non-inductive resistance R of low value, the coil under test C, here shown with a secondary, and an ammeter A. This is the usual circuit of a primary coil as used in gas engine ignition, the only difference being the use of a rotating break and the insertion of the extra resistance R. The former seemed preferable from the standpoint of uniformity of action, and the latter is necessary to obtain the curve of current. It has a resistance, however, of only 0.133 ohm, and in fact amounts to no more than the resistance of the usual wiring of a coil. The fact that we are here operating under actual working conditions is very important.

From points on the circuit as shown, connections are made to a row of mercury cups. By means of the fork-shaped arrangement shown just below the mercury cups, connection can be made to any part of the circuit. Thus taking them in order from left to right, we can connect with the battery, the break, the non-inductive resistance, the primary of the coil and the secondary of the same. With the primary is included the ammeter, which may be considered an extra inductance and resistance added to the coil. Its influence, however, is negligible.

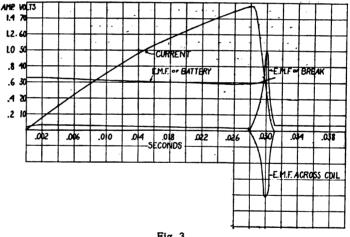
The contact maker marked C.M is of the usual form used in investigating E.M.F. waves. It is rigidly connected to the shaft of the rotating break and the whole is operated by a I H.P. motor. The current for the motor is taken from a storage battery. Thus the pressure and hence the rate of rotation are very uniform. Changes of speed are provided for by varying the number of cells connected to the armature. The field is kept constant. In this arrangement no resistance is used, hence the rotation at low speeds is much more uniform than would otherwise be possible.

S.R. (Fig. 2) is a shunt rheostat. This is used to give any desired potential difference from zero to that of the battery employed. In the actual setup, a slightly more complicated arrangement was used. It was necessary to have a variable voltage ranging from zero to about one hundred volts, and instruments capable of reading accurately any voltage in this range. This was accomplished by using two voltmeters, each having two scales. One was a milli-voltmeter giving a full scale deflection with 0.03 or 0.3 volt depending upon which scale was used. The other voltmeter had ranges of 3 and of 150 volts. Any one of these four scales could be readily connected as desired. For convenience in getting low voltages, two batteries instead of one as shown were used and either could be readily thrown in as desired. For a fine adjustment, a low adjustable resistance was used in series with the battery. This is also omitted in the figure. The instantaneous voltage across any part of the circuit can be balanced against the voltage at the terminals of the shunt rheostat, and the curves thus determined point by point. Current curves are obtained by measuring the voltages over the non-inductive resistance and dividing by the resistance.

This method while rather laborious, has four very important advantages over any other. The first is that the circuit is working under absolutely normal conditions, the resistance of R and that of the ammeter being no more than would usually be present in

Secondly the voltages are read directly and on ordinary practice. Therefore the accuracy is great, no computation is voltmeters. required and the chance of error is slight.

The third and greatest advantage is that absolutely no current is taken from the circuit in making the measurements. This follows of course from the fact that this is a balance method, the energy to operate the voltmeter being taken from the auxiliary battery. This is very important as the amount of energy carried is small and if any were required to operate the instruments, the error would be considerable.



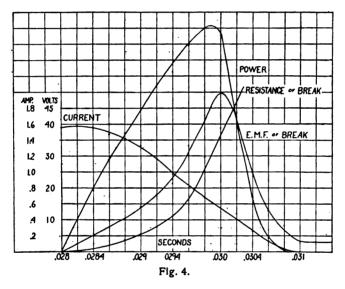


It should also be pointed out that changes in the force with which the brush of the contact maker presses on the rotating steel piece, do not affect the accuracy of the method. A poor contact has simply the effect of introducing a little extra resistance in the galvanometer circuit, but does not at all change the balance.

Let us now consider some of the results obtained. Fig. 3 shows

viously pointed out, follows the law  $i = I(1 - e^{-Rt/L})$ . The values of the constants were determined for this case and were as follows, E = 3.33, R (of entire circuit) = 1.276 and L = 0.0422. The curve that would be obtained using these values, differs inappreciably from the one in Fig. 3.

Near the top of the curve it bends over gradually. This is due to the fact that the brush is beginning to slide off from the contact, thus increasing the resistance. As soon as the break actually occurs, the current drops very rapidly and the curve is practically a straight line. This is seen better from Fig. 4. The fact that



the current during the break follows practically a straight line is of importance, as this assumption was made in the theoretical part of this investigation.

The curve of E.M.F. across the break is next in importance. From the moment of contact until the break begins to take place the potential difference is very small, amounting only to the product of the current and the resistance of the contact. It was accurately measured and found to increase according to the same law as the current, as was of course to be expected. The values, however, are too small to show in the curve. At the instant of the break, the stored magnetic energy of the coil is liberated and shows itself in the sudden and large rise in voltage. In this case the maximum voltage was 49.5 volts. After reaching its maximum it very rapidly drops to 3.33 volts, the E.M.F. of the battery, which is of course applied across the gap as long as the the circuit is open.

The curve of the E.M.F. over the coil is next to be considered. At the instant of make it jumps to approximately the E.M.F. of the battery, and then gradually decreases during the make. At the instant of break, the induced E.M.F. is suddenly reversed by the decrease of the lines of induction and a peak much like that of the Eb curve is produced, but in the opposite direction.

The last curve is that of the potential difference of the battery. It of course drops off gradually during the make as the current is increased and again rises during the break to its former value. Since the sum of all the E.M.F.'s in any closed circuit is zero, calling the E.M.F. over the non-inductive resistance Er, we should have Eb = Er + Ebr + Ec each being of course taken with its proper sign. This is a good test of the correctness of the work and as is seen from the curves is very accurately fulfilled.

In Fig. 4 two additional curves are plotted those of power and resistance of break. These are computed curves, the latter being obtained by dividing Eb by *i*. It of course starts from almost zero, and quickly rises, becoming infinite at the instant of complete break.

The other curve W is the curve of power. It is obtained by multiplying together the instantaneous values of current and E.M.F. during the break. The maximum of this curve is 31.4 watts. This is very important as it is probable that good ignition is dependent upon the maximum of this curve rather than upon its total area.

We are now in a position to solve our main problem, the determination of the efficiency. This may be obtained either for the whole circuit including the battery or for the coil alone. The former is slightly simpler and will be here considered.

The rate of input of energy is evidently Ei where E is the E.M.F. of the battery and i is the current. This lasts during both make and break. Since E is constant, the total input is simply (average i)  $\times E \times t$ , where t is time of both make and break. Here average i = 0.895 ampere, E = 3.33 volts and t = 0.0318 second. Hence  $W = 0.895 \times 3.33 \times 0.0318 = 0.0942$  joule.

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Similarly the output is given by (average ei)  $\times tb$ , in which e is the E.M.F. across the break only. Average ei is the same as average W, or the average of the curve W. This from the curve is found to be 16.41 watts, and tb = 0.00309 second. Hence the output is 0.0508 joule. Finally efficiency equals

$$\frac{\text{output}}{\text{input}} = \frac{.0508}{.0942} = 54.0 \text{ per cent.}$$

A comparison of this value with that obtained according to the theory previously developed is of interest. Calculating the various quantities by the method there explained we obtain the following where all quantities are expressed in joules :

Magnetic energy,	0.0514
Energy added during break,	0.0080
Eddy current loss during make,	0.00004
Eddy current loss during break,	0.0006
Ohmic current loss during make,	0.0385
Ohmic current loss during break,	0.0032
Hysteresis loss,	0.0010

Substituting in the formula for efficiency gives

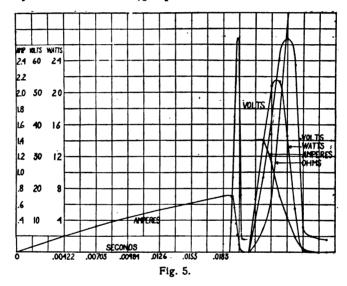
$$\eta = \frac{514 + 80 - 32 - 6}{514 + 80 + 10 + 0.4 + 385} = \frac{556}{989} = 56.2 \text{ per cent.}$$

This computed value agrees very well with the observed valueof 54 per cent.

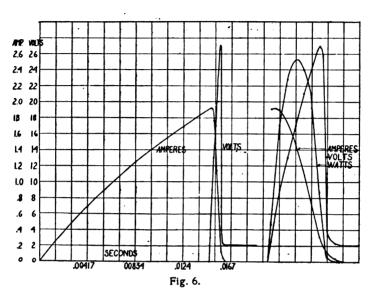
It should be pointed out that this coil was not operating under the best conditions. The energy in the spark, 0.0508 joule, was about three times as much as is needed for good ignition. Hence it would have been practicable to cut down very greatly the time of make. This would have reduced the ohmic loss of the coil, which as may be seen above is much greater than any of the others. With a contact of about  $\frac{1}{100}$  second the efficiency of the coil as was shown before is about 85 per cent.

Fig. 5 shows curves for another coil. This coil was much larger than the first one, contained more iron, and consequently had an inductance about twice as great. The resistance, however, was only slightly greater. The speed of the rotating break was increased so that the make was about two thirds as long as before. The influence of the inductance is clearly seen in the much slower rise of the current. The voltage at break on account of the high inductance and the quick break rises higher than before reaching 67 volts.

At the right are given on an enlarged scale the curves of volts, watts, amperes and ohms at break. These show the same general shapes as before. The input of the coil is of course less and the efficiency works out to be 43.2 per cent.



In Fig. 6 we have on the other hand the curves of a coil having an inductance of only 0.0121 henry; about one fourth of that of the coil of Fig. 3 and about one seventh of that of Fig. 5. This was operated with a voltage of only 2.072 that of one storage cell; in fact the coil was wound to test the possibility of operating a primary spark coil with a very low voltage. The time of make and break are about the same as in Fig. 4. The current rises very rapidly on account of the low inductance. The voltage at break, however is only about half as great as in the other two cases but



the primary. Under these conditions, the electrical actions are in all respects similar to those of the primary coil. To be sure the secondary winding has a certain capacity, and the E.M.F. induced in it causes a slight displacement of electricity. This effect is greatest in large coils wound with very fine wire, but even there it is entirely negligible. With coils for very high frequency, say in the neighborhood of 100,000 cycles per second, the case is entirely different, and this capacity may have a very decided effect upon the voltage produced. For the present we shall consider only coils in which the frequency does not exceed 1,000 cycles per second, and this effect will consequently be neglected.

For the coil then without condenser and whose secondary is open no farther investigation is necessary. Figs. 4 and 5 show all the actions taking place with the single exception of the curve of secondary E.M.F. This is, however, readily derived. Since we have assumed that there is no current in the secondary. it will obviously

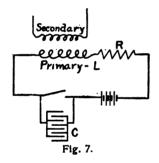
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ing the make. It starts with the value ME/L at t = 0 and gradually decreases, becoming practically zero for large values of t.

Most commercial induction coils are provided with condensers connected across the break. These serve in general two purposes. First, they prevent largely the arcing which would otherwise occur at the break and secondly they increase in general the E.M.F. induced in the secondary. In addition they may or may not set up oscillations in the circuits. We shall now examine these functions somewhat in detail.

During the make the condenser is short circuited and hence it has obviously no effect. We may then neglect this part of the cycle and concern ourselves with the break only. In general the - current during the break becomes oscillatory, and dies out gradually. If the break be instantaneous we have the following equations in which all the quantities refer to the primary.



$$L\frac{d^2q}{dt^2} + R\frac{dq}{dt} + \frac{q}{C} = E$$

where q is the quantity of electricity in the condenser, E is the E.M.F. of the battery and C is the capacity of the condenser. dq/dt is the current i and the equation is the same as before except for the term q/C. This is the potential difference over C the condenser. The ar-

rangement of the circuit is shown in Fig. 7.

The solution of the above well-known differential equation is

$$i = \frac{dq}{dt} = Qe^{at} [\omega \cos \omega t + a \sin \omega t]$$

where

$$a = -\frac{R}{2L}, \quad \omega = \sqrt{\frac{1}{CL} - \frac{R^2}{4L^2}},$$

and the time of one oscillation is given by

$$T = \frac{1}{n} = \frac{2\pi}{\sqrt{\frac{1}{CL} - \frac{R^2}{4L^2}}}$$

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INDUCTION COILS.

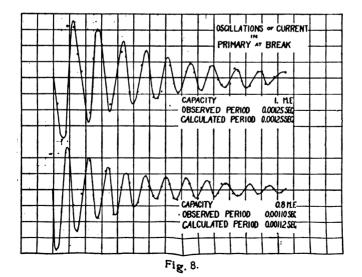
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Usually in practice  $R^2/4L^2$  is very small compared with I/CL and may be neglected. In this case we have  $T = 2\pi\sqrt{LC}$ . In practice  $\omega$  is usually of about the order 10<sup>3</sup> while  $\alpha$  is purposely kept low. Hence we may usually neglect the last term and we get  $i = Q\omega e^{\alpha t} \cos \omega t$ . It is evident that just at the instant of break  $i = i_b$ and since t = 0 we have  $i = Q\omega$  or substituting,

$$i = i_b \varepsilon^{-\frac{Rt}{2L}} \cos \frac{t}{\sqrt{LC}}$$

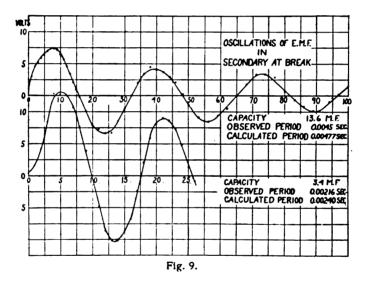
This means that the current oscillates with a gradually decreasing amplitude. In fact it dies out gradually in just the same way that it grows to its final value during make, but only half as fast.

The primary E.M.F. is given by  $L \cdot d^2q/dt^2$  as shown above and the secondary E.M.F. by  $M \cdot dq^2/dt^2$ . If as before  $\alpha$  is negligible compared to  $\omega$  we have  $e_p = LQ\omega^2 \varepsilon^{\alpha t} \sin \omega t$  and  $e_s = -MQ\omega^2 \varepsilon^{\alpha t} \sin \omega t$ . That is in case the decrement is small the E.M.F. and the current differ 90° in phase.



of I microfarad capacity. Points could be readily taken for a long distance on the curve as shown. The number that could be obtained was, however, limited by the rotating break closing the circuit again. The points were taken one degree apart and since the contact maker was revolving 393 times per minute this corresponded to  $60\,393 \times 720 = 0.000213$  second. The average length of a wave in Fig. 9 is 5.88 degrees or 0.00125 second or 8,000 complete vibrations per second. The resistance of the circuit was 1.28 ohms, and substituting in the formula we get as the calculated period 0.00125 second which is the same result as before.

The lower curve of Fig. 8 is a curve of primary current for the same coil but with a smaller capacity. The two curves of Fig. 9



are curves of secondary E.M.F. in the same coil. The frequency of oscillation is of course the same in the secondary as in the primary and the calculated and observed times show good agreement. These four curves with the exception of the lower one of Fig. 9 are all plotted to the same scale of time and illustrate well the great variation in frequency caused by the condenser.

In the remaining curves, in order to save time, only a few points near the beginning of the curve were taken, then the contact maker was moved ahead a certain number of degrees, the number of waves passed over counted, and a few more points taken. This supplied at least two crossings, and the number of waves between the crossings, and consequently all the data needed to determine the time of vibration were at hand. Table II. gives the computed

	TABLE II.	
Capacity in	Computed	Observed
M.F.	Time.	Time.
1.0	.000125	.000125
.8	.000116	.000110
.6	.000100	.000093
.4	.000082	.000078

and observed times for a number of different values of the capacity. It will be noted that in every case except the first, the observed time is less than the computed. This is probably due to the fact that, especially with small values of the capacity, there is some burning of the contacts at the break. This burning and roughening of the surface causes the break to occur earlier and consequently has the effect of moving the later points farther to the left than they should go, thus causing the apparent discrepancy.

EFFECT OF CAPACITY UPON THE SECONDARY E.M.F.

At the moment of break the energy stored in the coil is  $\frac{1}{2}Li_b^2$ and that in the condenser is zero. Assuming that there is no loss at the break, *i. e.*, no sparking, practically all of this is transferred to the condenser a quarter of a period later, from whence it again surges back into the coil and so continues until it is all dissipated in various losses. When the energy is stored in the condenser its value is  $\frac{1}{2}E_c^2C$  and since as explained above this is practically equal to  $\frac{1}{2}Li_b^2$  we may write

or

$$\frac{1}{2}E^2C = \frac{1}{2}Li_b^2$$
$$E_c = i_b \sqrt{\frac{L}{C}}.$$

But the maximum E.M.F. over the coil is the same as that over the condenser since they are directly connected together, hence we have for the primary

$$E_b = i_b \sqrt{\frac{\overline{L}}{\overline{C}}}.$$



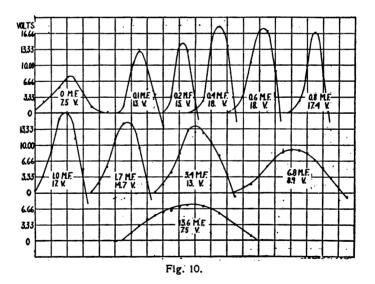
B. F. BAILEY. [Vol. XXVI.

If the magnetic leakage be neglected the primary and secondary E.M.F.'s are in the ratio of their respective turns or  $E_p/E_p = N_p/N_p$ . Hence we have as the final expression for the secondary E.M.F.

$$E_{a} = i_{b} \frac{N_{a}}{N_{p}} \sqrt{\frac{L}{C}},$$

and we see that both the primary and secondary E.M.F. vary inversely as the square root of the capacity.

On the other hand we have to consider the loss of energy in sparking at the break. It is of course evident that the E.M.F. across the break and that across the condenser are the same. The larger the condenser the lower the E.M.F. and the less the spark-



ing. It is then quite evident that we have here two conflicting elements and it appears probable at once that a compromise will give the best results. This is already known to be the case<sup>1</sup> and is shown very clearly in Fig. 10.

This figure shows curves of secondary E.M.F. for gradually

get a series of oscillations in the secondary. This is also the case in all the following curves, but to save space only the first half wave is shown. This in every case gave the greatest value of the voltage. The succeeding curves show increasing values of the E.M.F. up to a capacity of 0.4 microfarad and beyond this point they decrease regularly. In this particular case then 0.4 microfarad is the best capacity if maximum secondary E.M.F. be the only consideration. If efficiency also is to be considered, a larger value of the capacity would be desirable.

It is possible by means of the formula already derived to calculate the values of the E.M.F. that should be developed in the secondary at break. This is done by means of the formula

$$E_{\bullet} = \frac{N_{\bullet}}{N_{\bullet}} i_{\bullet} \sqrt{\frac{\overline{L}}{C}},$$

and it furnishes us with the means of computing the E.M.F. of any induction coil. To do this it is necessary to know the values of  $i_b$ , L,  $N_b$ ,  $N_p$  and C. These can, however, be readily measured in any particular coil.

In the case of the coil used in obtaining these curves, the current at break was 1.20 amperes, and the other values are as given before. In the case of the last curve of Fig. 10 we have

$$l_{e} = \frac{581}{504} \times 1.20 \sqrt{\frac{.0422}{.0000136}} = 7.70 \text{ volts.}$$

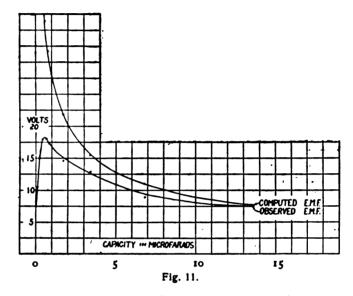
The observed value as shown by the curve is 7.5 volts, which agrees very well with the calculated value.

TABLE	III.

Speed of Breaking = 80 Inches per Second.					
Capacity in M.F.	Maximum Observed.	Computed E.M.F.			
0.0	7.5	infinity			
0.1	13.0	91.2			
0.2	15.0	64.4			
0.4	18.0	45.5			
0.6	18.0	37.2			
0.8	17.4	32.2			
1.0	17.0	28.1			
1.7	14.7	22.1			
3.4	13.0	16.5			
6.8	8.9	11.0			
13.6	7.5	7.8			

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In the same way the E.M.F.'s for the other values of the capacity were calculated. The results as well as the observed maxima of the waves are given in Table III. and the same quantities are plotted in Fig. 11. They show good agreement for the larger values of the capacity, the observed E.M.F. being always less than the computed one on account of the loss at the break. The dis-



crepancy becomes greater as the capacity becomes less, on account of the condenser being less able to suppress the sparking. It is apparent from the curve that if the object be to get the highest possible secondary E.M.F., *i. e.*, the greatest spark length, the condenser should have a value of 0.4 M.F. However with this capacity there is considerable sparking and the efficiency is rather low. Consequently for general purposes a somewhat larger capacity would be preferable.

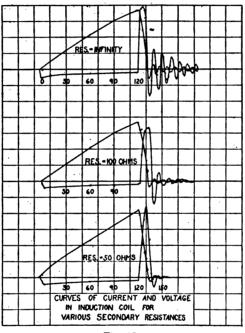
# EFFECT OF CURRENT IN THE SECONDARY.

So far in these experiments, no current has been taken from the secondary, that is the coil has been on open circuit. We have now to enquire into the changes that are produced in practice, when the secondary is used to supply current. Figs. 12 and 13 were taken to show the action in this case.

#### INDUCTION COILS.

The coil used had a core consisting of about 600, No. 16 soft iron wires, forming a bundle  $6\frac{3}{8}$  long by  $1\frac{3}{4}$  in diameter. The secondary and the primary each contained 252 turns of No. 13 wire. The secondary was wound outside of the primary and thus had a higher resistance. Otherwise they were alike.

This plan was adopted to keep the secondary E.M.F. within the limits of about 100 volts for the sake of ease of measurement.





The first curve of Fig. 12 shows the variations of secondary E.M.F. and primary current in the coil with open secondary. The primary current as before rises gradually, breaks and dies away in a series of oscillations of decreasing amplitude. The secondary E.M.F. at make jumps up almost instantly to its maximum make value. This value is practically equal to the battery voltage multiplied by the ratio of the secondary to the primary turns. The equation of this curve has been obtained and is

$$e_{a} = \frac{M}{L} E \varepsilon^{-\frac{Rt}{L}}.$$

If the leakage is small  $M = \sqrt{L_p L_i}$  where  $L_p$  and  $L_i$  are the inductances of the primary and secondary respectively; hence

$$e_{i} = -E \sqrt{\frac{\overline{L}_{i}}{L_{p}}} e^{-\frac{Ri}{L}},$$

and since the inductance is proportional to the square of the number of turns this becomes

$$e_{a} = E \frac{N_{a}}{N_{p}} e^{-\frac{Rt}{L}}.$$

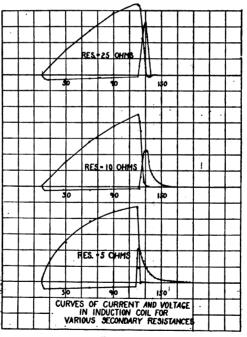


Fig. 13.

At t = 0 this becomes  $E \cdot N_i/N_p$  and decreases gradually as t increases, in fact approaching zero according to the same law as i

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current in the wrong direction. Here it would be well to keep E as small as possible. A coil used with a Wehnelt interrupter on a 110-volt or 220-volt circuit naturally gives much trouble from inverse current on this account. Such a coil should work much better on an alternating than on a direct current, since the current would in general not rise so rapidly.

At the break the conditions are quite different. We have shown that here we have

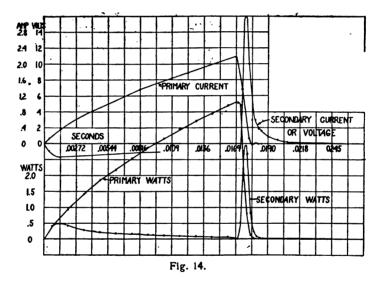
$$i = i_b \varepsilon^{-\frac{Rt}{2L}} \cos \frac{t}{\sqrt{LC}}$$
 and  $e_s = -Mi_b \frac{1}{\sqrt{LC}} \varepsilon^{-\frac{Rt}{2L}} \sin \frac{t}{\sqrt{LC}}$ .

These equations show that both the primary current and the secondary E.M.F. will die out in a series of oscillations, the rate of dying out, *i. e.*, the logarithmic decrement will be half that of the current and E.M.F. at the make since here the coefficient was  $e^{-Bt/L}$ . Moreover the current and E.M.F. will be so related to one another that one will be zero when the other is a maximum, *i. e.*, they differ 90° in phase. All these conclusions are verified from the curves and are all obvious except the second. To show this let us examine the ratio of the maxima of the two successive E.M.F. waves. For this we may take  $\omega t = 0$  and  $\omega t = 2\pi$  or t = 0 and  $t = 2\pi/\omega$ ; we then have

$$\text{Ratio} = \frac{-Mi_{b}\omega\varepsilon^{-Rn/L}}{-Mi_{b}\omega\varepsilon^{-Rn/L}} \sin \frac{O}{2\pi} = \frac{\varepsilon^{-0}}{\varepsilon^{-Rn/L}} = \varepsilon^{\frac{Rn}{L}} = \varepsilon^{\frac{Rn}{L}} \sqrt{\frac{C}{L}}.$$

This then should be the ratio of two successive waves and substituting the values of the quantities we have Ratio  $= 2.72^{.0591} = 1.04$ . Hence each succeeding wave should be about 4 per cent. lower than the preceding one. The actual decrease is about 25 per cent. instead of 4 per cent. The difference is largely due to the loss in eddy currents which act just like a load on the secondary.

As soon as current is taken from the secondary the conditions change. The solution of the equations becomes quite complicated and will not be given here.<sup>1</sup> It is evident however, that if the secdary would tend to oscillate in the same way that that in the primary does. The two currents would not necessarily have the same frequency nor the same decrement. Owing, however, to the mutual action of the primary and secondary, both currents would take up an oscillation which would be the sum of two oscillations of different frequencies and decrements. In the case of a secondary connected to a non-inductive resistance, the secondary current of itself will not oscillate.



Hence, on account of the mutual induction of the two coils it will tend to prevent the primary current from oscillating. This action of the secondary current will obviously be the more powerful the less the secondary resistance, that is, the greater the secondary current.

Figs. 12 and 13 show the effect of increasing gradually the current taken from the secondary. The resistance used was non-induc-

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In the second curve of Fig. 12 with 100 ohms secondary resistance oscillations are present although much reduced and in the third curve for which the secondary resistance was 50 ohms this reduction is still more marked. In the curves of Fig. 13 with respectively 25, 10 and 5 ohms the oscillations have disappeared although a slight trace is still present in the primary current. It will be noted that the secondary E.M.F. and current attain their maximum values at about the time the primary current becomes zero. It is evident that the magnetism of the core is not zero, being maintained by the secondary current, and this magnetism now proceeds to dissipate its energy, by producing current in the secondary. In fact there is no other way for it to be dissipated, providing oscillations are not present, when it would be largely wasted in eddy currents and  $I^3R$  losses.

In the induction coil employed as it usually is to produce a spark, the curves would be somewhat different. In general no current would flow during the make, and the curve of decrease of current would be somewhat steeper, since the resistance depends upon the current flowing.

We may regard the induction coil from a slightly different standpoint. By considering only the case most frequently met with in practice, that of a non-inductive receiving circuit without capacity, the theory becomes simpler. If we further suppose that the receiving circuit has a low enough resistance so that oscillations are entirely prevented, it becomes possible to present the entire theory of the coil in a very definite and simple form, the only uncertainty being that connected with the action during the break. This period is very short compared with the duration of the break current of the secondary. The theory of the coil under these circumstances has been treated by Fleming in the book before referred to and it is there shown that during the make the currents are represented by

$$i_{p} = I - \frac{I}{2} \left( \varepsilon^{-\frac{Rt}{L+M}} + \varepsilon^{-\frac{Rt}{L-M}} \right)$$

and

$$i_{\epsilon} = -\frac{I}{2} \left( \varepsilon^{-\frac{Rt}{L+M}} - \varepsilon^{-\frac{Rt}{L-M}} \right).$$

The inductance of the primary and secondary are here considered as equal.

During the break some uncertainty exists. If, however, the break be assumed to follow a straight line law, and this seems to be amply justified by the curves taken, we have the very simple equation,

$$\mathbf{o} = R_i \mathbf{i}_s + L \frac{d\mathbf{i}_s}{dt} + M \frac{d\mathbf{i}}{dt}.$$

Since we represent *i* as before by

$$i = i_b - \frac{t}{T}i_b$$
,  $M\frac{di}{dt} = -\frac{i_b}{T}$ .  $M = a$  constant.

Hence

$$M \; \frac{i_{\bullet}}{T} = R_{\bullet}i_{\bullet} + L \frac{di_{\bullet}}{dt},$$

is the equation of the secondary circuit. This is the ordinary Helmholtz equation and its solution is

$$i_{\mu} = \frac{Mi_{\mu}}{TR_{\mu}} \left(1 - e^{-\frac{R_{\mu}}{L_{\mu}}}\right).$$

To find the value of  $i_i$  at the instant of complete break we have only to substitute t = T. We are especially interested in the case when the time of break T is very nearly zero. The expression for  $i_i$  becomes of the form 0/0 for T = 0, hence writing

$$i_{\bullet} = \frac{Mi_{\bullet}}{R_{\bullet}} \cdot \frac{(1 - \varepsilon^{-R_{\bullet}T_{1}L_{\bullet}})}{T}$$

and differentiating both members we get

$$\frac{R_{e}}{L_{e}} \varepsilon - \frac{\frac{RT}{L_{e}}}{1} \frac{Mi_{b}}{R_{e}},$$

which for T = 0 is equal to

$$\frac{Mi_b}{R_b} \cdot \frac{R_b}{L_b} = \frac{Mi_b}{L_b} \cdot$$

If as is very nearly the case

$$M = \sqrt{L_s L_p}$$
 and  $\frac{L_s}{L_p} = \frac{N_s}{N_s^2}$ 

we may write

$$i_{sm} = \sqrt{\frac{\overline{L}_{p}}{\overline{L}_{s}}} \cdot i_{b} = \frac{N_{s}}{N_{s}} i_{b}.$$

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#### INDUCTION COILS.

This result might have been obtained more simply by consideration of the energy involved. The work stored in the primary at the instant of break is  $\frac{1}{2}L_{p_{b}}i^{2}$ . If the break be instantaneous and hence no energy be wasted in the process, all this energy must be transferred to the secondary. We then have at once

$$\frac{1}{2}L_{p}i_{b}^{2} = \frac{1}{2}L_{c}i_{c}^{2}$$
 or  $i_{c} = \sqrt{\frac{L_{p}}{L_{c}}}i_{b}^{2}$ 

This is a rather surprising result at first sight, since the E.M.F. is independent of the capacity of the condenser and of the resistance in the secondary circuit. Moreover, it depends upon the inverse ratio of the turns  $N_p/N_o$ . It should be contrasted with the expression for the E.M.F. at break

$$e_{\rm sm} = \frac{N_{\rm s}}{N_{\rm p}} i_b \sqrt{\frac{L_{\rm p}}{C_{\rm p}}}.$$

This arises from the fact that while the E.M.F. generated is in proportion to  $N_{e}$  the inductance of the secondary at the same time increases in proportion to the square of  $N_{e}$  and hence an increase in  $N_{e}$  actually means a decrease of the maximum momentary current.

It is a fact that many makers of large induction coils for X-ray work are winding the secondaries with much coarser wire than formerly and the users claim that such coils pass much more current in the proper direction and much less inverse than those of the conventional design.

When the break is completed the influence of the primary upon the secondary ceases almost entirely. We have then merely to consider the dying away of a current in an inductive circuit. The equation is  $0 = R_{i_s} + L_s di_s/dt$ . The well-known solution of this is  $i_s = i_{sm} e^{-R_s t/L_s}$ . Theoretically this would require an infinite time for the current to die away. As may be seen by Figs. 13 and 14 the actual time was comparatively long, and traces of current could be detected for some time beyond that shown.

The curves of Figs. 13 and 14 confirm the preceding theory very closely, with the possible exception of that relating to the current during break. The E.M.F. generated during this time is so great and the consequent rise of current is so rapid that it is difficult to follow it. However, as nearly as can be seen from the curves, the shape is apparently that called for by the theory.

#### Efficiency.

The efficiency of an induction coil may be obtained in the same way as in the case of the primary coil. An examination of the curves of Figs. 11 and 12 indicates that the maximum secondary output will be obtained with some value of the secondary resistance between 5 and 10 ohms. It was estimated that 8 ohms would probably be the resistance giving the greatest output and the curves of Fig. 13 were taken with this value. The upper curves, those of primary current and secondary voltage, were taken directly. The curves of watts in the primary and secondary were computed from the readings, the points of the secondary watts being given by  $E_{e}^{2}/R_{e}$ . This latter would not be possible had R not been noninductive. It should be noted that the secondary watts at the break are plotted on a scale only one tenth as great as is used in the other curves. It is interesting to note that just after the make the curve of secondary watts rises almost as fast as that of primary watts, or the output is almost as great as the input. Hence the efficiency is high and the relative amount of energy delivered during the make is great. If it is desirable to get as much energy as possible from the coil during the make, the contact should be short and the battery voltage high. The usual requirement is just the reverse of this, as was pointed out, but for medical coils, such a distribution of energy between the make and break is frequently preferable.

The efficiency is readily obtained from the curve by dividing the area under the curve of secondary watts by that under that of primary watts. This gives here the following results:

Input during make,		0.0417 joule
Input during break,		0.0032 joule
Output during make,		0.0031 joule
Output during break,		0.0193 joule
Total input,		0.0449 joule
Total output,	•	0.0224 joule

The efficiency is then .0224/.0449 or 50 per cent.

to all other than the second sec



not be greatly affected and the resulting efficiency would be 0.0193/0.0449 or 43 per cent.

In any given coil it is possible to predetermine, to a certain extent the output, at least we can set an upper limit to the energy of each spark, and thus compare the igniting power of various coils. This follows from the fact that the energy in the spark cannot possibly exceed the stored magnetic energy of the coil. That is, it cannot exceed  $\frac{1}{2}Li_b^3$ . L and  $i_b$  are determined in the manner previously explained. For example in the present case

 $\frac{1}{2}Li_b^2 = \frac{1}{2} \times 0.0121 \times 2.18^2 = 0.0288$  joule.

The measured output was 0.0193 joule or about 67 per cent. of the possible output.

On the other hand the input during make will of course be larger than the stored magnetic energy. In this case they are in the ratio of 0.0288 to 0.0417 or of the energy put in during wake, about 70 per cent. is stored as magnetic energy.

To recapitulate, by measuring for any coil the five quantities R,  $\mathcal{L}$ , C,  $i_b$ ,  $N_a/N_p$ , or the resistance, capacity, current at break and ratio of primary to secondary turns we can determine the four principal characteristics of the coil. Its secondary E.M.F. is given by

$$E_{a} = i_{b} \frac{N_{a}}{N_{p}} \sqrt{\frac{L}{C}},$$

its maximum output per spark by  $\frac{1}{2}Li_b^2$ , its frequency of oscillation by  $n=2\pi\sqrt{LC}$  and the maximum current at break by  $i_{sm}=i_b\cdot N_{p'}/N_s$ .

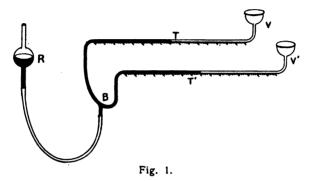
## A DIFFERENTIAL VOLUMENOMETER.

## BY ALBERT P. CARMAN.

THE volumenometer or stereometer, invented by the French military engineer Say in 1797,<sup>1</sup> remains in some of its forms, the only instrument for determining the volumes of small irregular bodies and powders which cannot be immersed in a liquid. The fundamental principle of all volumenometers is the determination from Boyle's law of the volume of air imprisoned in a space V by observing the change of pressure corresponding to a given change of volume. The volume is changed in all forms by raising and lowering mercury in a graduated tube, the upper part of which is the vessel V. Then placing the body of volume x in the same space V, the new volume of air is found, and thus by subtraction, the volume x of the body is gotten. Most of the five or six volumenometers<sup>2</sup> which have been described and used in scientific work, differ simply in the methods of raising and lowering the mercury, that is, in the means of changing the volumes and measuring the change. In the volumenometer of Oberdeck we have an instrument which is distinct from previous forms in being differential. It was from a study of Oberdeck's instrument that the present work started. The first form described below was started simply as an improved form of Oberdeck's instrument, but it was found to have some new features both in theory and manipulation, and this led to experiments with modifications, as will be described.

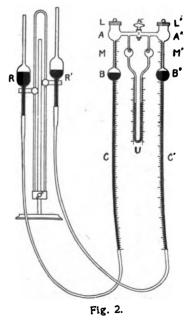
Oberdeck's form is shown in Fig. 1; V and V' are two equal glass cups which can be closed by ground-glass plates;  $\dot{T}$  and T'

reservoir R. By raising and lowering R, the volume of air imprisoned in V and V' can be changed. An essential feature of Oberdeck's instrument is that the pressures on the two sides are



always equal, since the two tubes are on the same level. The increments of volume are read by the position of the mercury columns  $\cdot$ in the graduated tubes *T*. Some experiments showed that there

must be considerable error in such readings owing to the lag of the mercury in horizontal tubes. It is also evident that the tubes T must be made long to get great sensitiveness, since the device of enlargements is not possible in horizontal tubes. To improve these features the instrument shown in Fig. 2 was made. A and B are vessels, each of about 5 c.c. capacity. A lid Lcan be clamped air-tight on A. Mis a glass tube connecting A and B. C is a graduated glass tube. This tube is connected by rubber tubing with a mercury reservoir R. This reservoir can be raised and lowered so as to change the volume of the air imprisoned in AMRC. On the



a light aniline liquid. A stopcock K allows the ready equalizing of the pressures on the two sides. The whole is mounted on a vertical board; on the same base is a vertical rod to which the platform carrying the mercury reservoirs is clamped. The reservoirs R and R' can be moved separately on rods carried by the common platform. In the first instrument made the vessels A and B were turned out of steel because they could be thus made exactly equal on the two sides. This equality is necessary in Oberdeck's method. Making these vessels of steel involved sealing them to glass and this caused more trouble and delay than anything in these experi-The volumenometer proved a very sensitive method of dements. tecting air leaks. An instrument has now been made all of glass with mercury sealed joints. This has solved the leak trouble.

The manipulation and theory are as follows: With the cups A open to the air the mercury is raised to the marks M and the vessels are then closed. Air is thus imprisoned at atmospheric pressure. The mercury reservoirs are lowered allowing the air volumes V and V' to expand by increments DV and DV' respectively. But during the operation the pressures on the two sides are kept equal by watching the manometer U. Letting p and p' represent the initial and final pressures, we have the relations

$$Vp = (V + DV)p'$$
 and  $V'p = (V' + DV')p'$ .

The mercury is next raised, restoring the volumes V. A body of volume x is now placed in A. The mercury is again lowered, keeping the pressures equal on the two sides, and giving the air in A, the previous increment DV. This will correspond to an increment DV'' on the right side for equality of pressure p''. We have then

(V-x)p = (Vx - x + DV)p'' and V'p = (V' + DV'')p''.

From the above we have

$$x = \frac{VDV'' - V'DV}{DV''}.$$

This is similar to Oberdeck's formula. It is believed that the vertical tubes and the sensitive method of determining equality of pressure on the two sides are an advance.

In working with the above volumenometer, an easier method of manipulation, using a simpler formula suggested itself. Starting as before, we have the relations

$$Vp = (V + DV)p'$$
 and  $V'p = (V' + DV'')p'$ .

After introducing the body of volume x, we increase the volumes keeping the pressures equal on the two sides, but giving to V' on the right side the previous increment DV'' and getting on the left the new increment DV'. Evidently the pressure is the same p' as above. We thus get

$$(V-x)p = (V+DV'-x)p'$$
 and  $V'p = (V'+DV'')p'$ .

Substituting for Vp and transposing we get

$$x = \frac{p'}{p - p'} (DV' - DV).$$

The difference of volume increments (DV' - DV) is read off in terms of scale divisions of the tube C. The factor p'/(p - p') can be determined directly from the pressures or it can be determined experimentally by placing a body of known volume in A and thus calculating it. This calibration has of course to be done at least once for each series on account of temperature and pressure changes, and the results are then read off direct in scale divisions of the tube. It is to be noted that no assumptions are made here of an equality of volume of the two sides. In getting the volume of turned brass cylinder, which could be accurately calipered, the results were 2.228 c.c. by the volumenometer and 2.210 c.c. by calipering. A steel ball was used for a standard. This shows the accuracy that has been attained ordinarily.

The above experiments were made in the summer and fall of 1906. In *Science Abstracts* for January, 1907, A. Lo Surdo's differential volumenometer is described. This has something of the appearance of the differential form described above, but it is in fact quite different in construction and manipulation.

UNIVERSITY OF ILLINOIS,

December, 1907.

## THE VARIATION OF APPARENT CAPACITY OF A CONDENSER WITH THE TIME OF DISCHARGE AND THE VARIATION OF CAPACITY WITH FREQUENCY IN ALTERNATING CURRENT MEASUREMENTS.

#### By B. V. HILL.

T has been known that the impedance offered by a condenser to the passage of an alternating current depends upon the frequency of the current. The capacity is larger for low frequencies than for high, but the amount of this variation was not so generally known. A writer in the American Telephone Journal for September 29, 1906, stated that the paper condensers ordinarily used in telephone circuits often fall 50 per cent. below their rated capacity, and that the capacity varies greatly with the frequency of the current applied. The manufacturing companies only warrant an accuracy of 10 per cent. for apparatus of this kind, so a slight change of electrical constants with frequency is not a very serious matter --- a dirty plug or a bent spring might make more difference in speech transmission than a small change in inductance or capacity in the circuit. It is of considerable importance, however, to be sure that a condenser rated at 2 M.F. really has that capacity and not merely half that amount. Several months ago Mr. Anthony Zeleny showed that the apparent capacity of a condenser, determined by the ballistic method, depended upon the period of the galvanometer, that is, upon the time during which the discharge of the condenser was to affect the needle or coil of the instrument. I decided to study the behavior of several condensers both with reference to their straight discharge and their capacity when a part of an alternating current.

For this purpose there were at hand six condensers of different kinds. They were, as designated below : (1) a Leeds and North-rup standard mica condenser of 1 M.F. capacity; (2) a Queen and



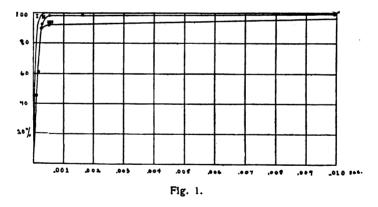
Company's paper condenser of I M.F. capacity; (3) and (4) telephone condensers of one firm rated at 2 M.F. capacity; (5) a telephone condenser of another firm rated at 2 M.F. capacity, and a sixth made by the same firm as (3) and (4) but of so low insulation resistance that no results could be obtained with it.

The straight discharge was first studied, the method being to charge the condenser for 20 seconds and then, after a period of insulation of about .07 second to connect to the ballistic galvanometer for times varying from .0001 second to 11 seconds, the quarter period of the galvanometer. To measure the times of connection with the galvanometer, two pairs of keys, a makeand a break-circuit key in each pair, were made and mounted on heavy maple blocks faced with ebonite. These keys were very similar to those ordinarily used in such experiments and described in the texts on electrical measurements, and so need not be described in detail here. Instead of the heavy pendulum ordinarily employed to release the keys, I mounted a 7/8" cold drawn steel rod in a vertical position near a strip, also vertical, upon which the keys were mounted. A weight sliding upon this rod struck the triggers and released the keys. The positions of the triggers were determined by means of a fine cathetometer. The friction of the weight upon the rod was first carefully determined and taken into account in computing the time between the setting off of the two triggers. The break-circuit key on each block was provided with a screw by which it could be moved with reference to the makecircuit key by very small amounts. The zero setting was approximated by finding a place where there was no throw of the galvanometer when the weight was released, but, if the breaking key was moved downward by the smallest possible amount, a throw was observed. Settings agreeing to I/6,000 of a second could thus be made. This does not represent the accuracy of the apparatus but the smallest distance through which the fingers could turn the screw. A series of readings was now taken. The condenser was first allowed to charge for 20 seconds. The weight was then

were plotted as abscissæ and the corresponding throws of the galvanometer as ordinates. The curve thus obtained was produced back across the axis of times and the point where it cut this line was taken as the true zero point.

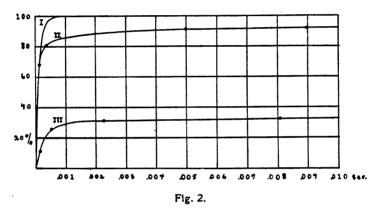
The galvanometer was a Leeds and Northrup type P d'Arsonval. It had a resistance of 127 ohms and an inductance of .0014 Henry. The coil was loaded with two small bullets so that its period was 43.08 seconds.

The behavior of the four condensers which were tested is shown, for times up to .01 second in the figures. Curve I. in the first figure is the theoretical discharge curve for the capacity of one microfarad and the corresponding curve of the second figure is the theoretical curve for the capacity of two microfarads. Curves II. and III., Fig. 1, refer to the Leeds and Northrup mica condenser and the Queen paper condenser respectively. With the former the effect



of absorption is over in a very short time but, even here, the galvanometer must have a period of at least 5 seconds if the complete charge is to be liberated. Using a Kemp's key with the ballistic galvanometer, the calculated capacity of this condenser was 1.0328 M.F. With the paper condenser the throw, after 8 seconds connection, is still 2 per cent. below that obtained with the Kemp's key and the capacity calculated from this full throw was 1.0519. These values may seem absurdly high, especially for so fine a piece of

component H and the value of this constant was uniformly lower than that obtained by Gauss' method, by an amount corresponding to the excess of capacity just shown in the condensers. From the results obtained in the alternating current measurements, the mica condenser appears to be very accurate and the fault is with the ballistic method of measuring the capacity.

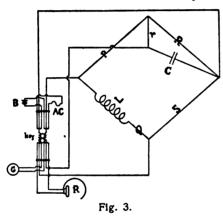


Curves II. and III. of the second figure refer to condensers (3) and (4), both being 2 M.F. paper telephone condensers. The capacity of a given condenser of this type increases, of course, with the amount of pressure applied in the making, while the insulation resistance decreases. That designated as (3) is of high resistance and is what they rate as a "hard" condenser; (4) is a medium, while the sixth one referred to in the beginning of this paper as giving no proper result at all, is called "soft." No. 3 appears to be a very good condenser of its class but (4) has parted with only about half of its charge at the end of .OI and is found to continue discharging for two minutes or more.

For determining the capacity of the condensers by means of alternating currents, it seemed best to use some method of comparing their impedance with that caused by a self-induction; for, even if there should be a small error in the value assumed for the latter,

## B. V. HILL.

effect of frequency upon resistance and inductance, for frequencies up to 3,000, is too small to be taken into account here. After trying several of the standard arrangements for comparing a capacity to an inductance a modification of Anderson's method was used. This involved the fewest assumptions and will allow a large number



of measurements to be made in rapid succession. The arrangement shown in Fig. 3 is the common one except that, by means of a double key, each half having six points, a battery and a galvanometer, or a source of alternating current and a receiver, may be connected to the points of the bridge by merely throwing the lever. Leaving the key in the

normal position, as shown in the figure, one may adjust the arms of the bridge for a direct-current balance and then, throwing the key into the other position, adjust the resistance r till the sound in the receiver is a minimum. The capacity is now given by the equation

$$C = \frac{L}{r(Q+S) + PS}.$$

To secure alternating current of varying frequencies up to 3,000, which was sufficiently high to represent ordinary voice currents, a small inductor-alternator was constructed. It consisted of an ebonite disk having about its circumference 60 soft iron, cylindrical inductors .25 in. in diameter, rotating between the poles of the field magnet. The armature coils were wound upon these poles. As the whole

Condenser.	Capacity (Ball).	Frequency.	Capacity.	Per Cent. Loss
1	1.0328	66	0.9961	
		125	0.9970	
		1,450	0.9951	
		2,945	0.9931	0.4
2	1.0519	16	0.9985	
		125	1.0005	
		1,360	0.9965	
		3,020	0.9901	0.8
3	2.170	16	2.0328	
		125	2.0367	
		990	2.0245	
		3,040	2.0064	1.49
4	2.170	16	1.8519	
		125	1.8519	
		1,350	1.8379	
		3,050	1.8046	2.55
5		16	2.3448	
		125	2.3420	
		1,350	2.3231	
		3,000	2.3066	1.10

tried. The worst, however, decreases but 2.55 per cent., which is an amount too small to be of account in considering their effect upon speech currents. As the frequency rises, the minimum of sound in the receiver becomes less marked in all cases. With the poorer paper condensers, this is true to such an extent that no very exact adjustments could be made, but the capacity of these condensers was somewhat indefinite.

It will be seen by comparing the discharge curves of the several condensers with their alternating-current capacities as given in the table, that the latter cannot be inferred from the former. Taking condenser No. 4, as an example, it will be seen that, up to .01 second, the capacity is only about 37 per cent. of that obtained when the condenser was allowed to discharge for the whole quarter period of the galvanometer. With an alternating current, however, in which the period of charge — that is, the quarter-period of the complete oscillation — was only .00008 second, the capacity was still 80 per cent. of that obtained by the ballistic method and the complete quarter-period of the galvanometer.

CHICAGO,

December 30, 1907.

THE AMERICAN PHYSICAL SOCIETY. [Vol. XXVI,

## PROCEEDINGS

#### OF THE

## American Physical Society.

MINUTES OF THE FORTIETH MEETING.

A REGULAR meeting of the Physical Society was held at Columbia University, New York City, on Saturday, February 29, 1908.

At the afternoon session, President Edward L. Nichols delivered an address on "Theories of the Color of the Sky."

The following additional papers were presented :

A Study of Anomalous Dispersion by Means of Channeled Spectra. S. R. WILLIAMS.

A New Form of Interferometer. C. W. CHAMBERLAIN.

Some Properties of Light of Extremely Short Wave-length. THEO-DORE LYMAN.

The Variation of the Thermomagnetic Effect in Soft Iron with the Strength of the Magnetic Field and with the Temperature Gradient. L. L. CAMPBELL.

The Kinetic Energy of the Negative Ions from Hot Metals. O. W. RICHARDSON and F. C. BROWN.

A Development of Wiedemann's Theory of Luminescence, with especial reference to the Decay of Phosphorescence. ERNEST MERRITT.

A Curious Ionization Effect in Vacuum Tubes. H. A. PERKINS.

Exhibition of a New Form of Colorimeter. F. E. IVES.

A Sine-wave Electrical Oscillator of the Organ Pipe Type (with demonstration). FREDERICK K. VREELAND.

The Origin and Life of Radium. BERTRAM B. BOLTWOOD.

Heat Developed in a Mass of Thorium Ovide due to its Radioactivity

## NOTES ON SUPERHEATED STEAM.<sup>1</sup>

#### BY HARVEY N. DAVIS.

1. On its Specific Heat at Constant Pressure. — This note discusses the available data, and in particular the papers of Knoblauch and Jacob, of the Technische Hochschüle in Munich, and of Thomas, of Sibley College, Cornell, and leads to the conclusion that in the two respects in which these papers are in serious disagreement, the results of Knoblauch and Jacob are to be preferred.

2. On its Total Heat. - During the last ten years several careful sets of "wire-drawing" experiments have been undertaken in the hope of computing  $C_{n}$  from them by means of Regnault's values for the total heat of saturated steam; but, as was pointed out by the experimenters themselves, this procedure is extremely sensitive to errors in Regnault's table, so that the resulting values of  $C_p$  are not to be compared with those since obtained by direct calorimetry. It is the purpose of this note to point out that the work of Knoblauch and Jacob makes it possible to reverse this process so as to obtain, not indeed absolute values, but a knowledge of the variation of the total heat with temperature in the range from 100° C. to 180° C. which is more trustworthy than anything previously reported. The original data of Grindley, Peake and Griessmann have been reduced from this point of view and the resulting curves show an unexpectedly satisfactory agreement. The average temperature coefficient from 100° to 180° is very nearly the well known 0.305 of Regnault, but all three lines show an unmistakable curvature, being concave on the side toward the temperature axis. A similar result has been deduced by Linde from the measurements by Knoblauch, Linde and Klebe of the specific volume of saturated steam. All three sets of observations are well represented by the empirical formula

 $\lambda = \lambda_{100} + 0.3745(t - 100) - 0.000990(t - 100)^{2}.$ 

Since all three curves are well defined near  $100^{\circ}$  (and one of them, indeed, down to  $60^{\circ}$ ) an attempt was made to connect up with the absolute determinations at these lower temperatures so as to get at absolute values throughout the range under consideration, but the outstanding discrepancy of nearly two calories between Regnault and Henning at  $100^{\circ}$  makes this somewhat uncertain. The only previous determinations above  $100^{\circ}$  are the experiments of Regnault and the computations of Linde.

3. On its Joule-Thomson Effect. — Buckingham in a very interesting paper recently published by the Bureau of Standards, follows several

<sup>1</sup>Abstract of a paper read before the American Physical Society, in New York, February 29, 1908.

earlier writers in basing an evaluation of the absolute thermodynamic scale upon the very reasonable assumption that the law of corresponding states applies to the Joule-Thomson effect in air, oxygen, nitrogen and hydrogen. He further assumes that it applies also to carbon dioxide, but the dependence of his thermometric conclusions upon this second assumption is probably so indirect that our confidence in them ought not to be much shaken even if it turns out that  $CO_3$  does not belong in the same group with the diatomic gases, provided that the law of corresponding states holds for them. It should be remembered, however, that this law has never been proved experimentally for any pair of them whatever, so that, although we accept Buckingham's results with confidence, nevertheless, an experimental investigation of the whole subject, and in particular of the possibility of classifying all sorts of substances on the basis of a law of corresponding states, is much to be desired.

It is the purpose of this note to make a small contribution in this field by evaluating the Joule-Thomson effect in H<sub>.</sub>O and comparing it with that in CO. The comparison is interesting as being the first of its kind, for carbon dioxide is the only gas for which we have hitherto had anything more than isolated values of the Joule-Thomson effect. For the evaluation for water vapor there are available, (1) the "wire-drawing" experiments already mentioned, which give about fifty direct experimental determinations, (2) some wire-drawing data at very high temperatures, hitherto unpublished, which have recently been generously put at my disposal by Mr. A. R. Dodge of the General Electric Company, and (3) the curves of constant "total heat content" that can be computed from the results in the first two of these notes. The resulting "reduced" values, when plotted, form a band which, although wider than might be wished, is quite definite enough for the present purpose, and which forms a surprisingly good continuation of a smooth curve through Kester's values for carbon dioxide. This confirmation of the law of corresponding states is the more striking because water is so anomalous in other ways that even a complete failure of the law would not have been A fortiore is it to be expected that the thermometric gases surprising. will satisfy the law.

I have examined all of the available data on steam for a possible varia-

## THE KINETIC ENERGY OF THE NEGATIVE IONS FROM HOT METALS.

#### BY O. W. RICHARDSON AND F. C. BROWN.

THE kinetic energy of the ions has been measured by observing the rate at which the potential of one of a pair of parallel plates charged up when a small area (about one square millimeter) of the opposite plate was occupied by heated platinum foil. The hot platinum and the plate surrounding it were maintained at zero potential. If the particles are shot off from the foil with a velocity component u perpendicular to the plates they will only reach the upper plate provided  $\frac{1}{2}mu^3 > Ve$  where m is their mass and e their electric charge, V being the difference of potential between the plates. The method thus measures the number of particles whose component of energy in the direction perpendicular to the plates (if we may be allowed to use this expression) is greater than a given value. It is evident that the results give the average value of this part of the energy and also the way in which it is distributed among the different particles emitted.

On the assumption that the ions shot off from the hot metal behavelike the molecules of a gas it can be shown that the number n which reach the upper plate against a potential V is given by  $n = n_0 e^{-\nu V e/R\theta}$ . where  $n_{0}$  is the number which reach the upper plate when V = 0, v is the number of molecules in 1 c.c. of a gas at normal temperature and pressure,  $\theta$  is the absolute temperature and R is the constant in the gas equation  $pv = R\theta$ . This formula is equivalent to  $\log i - \log i_0 = -vVe/R\theta$ where *i* and *i*, are the currents corresponding to *n* and *n*<sub>0</sub>. This has been tested by plotting the experimental values of  $\log i$  and V and the linear relation demanded by theory has been accurately verified. The inclination of this line is equal to  $ve/R\theta$ . Now ve is the quantity of electricity required to set free half a cubic centimeter of hydrogen at o° C. and 760 m.m. pressure by electrolysis. Substituting the value of this constant and that of  $\theta$  the temperature of the wire we find the value of R, the gas constant for the negative electrons. Different experiments. have given values ranging from  $3.5 \times 10^{3}$  to  $4.05 \times 10^{3}$  as compared with the standard value  $3.7 \times 10^3$ .

We are thus led to the conclusion that the kinetic energy of the negative electrons emitted by hot metals is the same as that of the translational kinetic energy of the molecules of a gas at the same temperature as that of the metal.

If we admit the truth of the atomic theory and the correctness of the accepted values for the mass of an atom this investigation furnishes what

<sup>1</sup>Abstract of a paper read before the American Physical Society, in New York,. February 29, 1908.

we believe to be the first direct test of certain theorems in the kinetic theory of gases relating to the way in which the velocities are distributed among the different atoms.

It is also suggested that a method based on these principles will ultimately be of value, on account of its practical simplicity and theoretical directness, as a standard of thermometry for very high temperatures.

PRINCETON, N. J.,

410

February 28, 1908.

## HEAT DEVELOPED IN MASS OF THORIUM OXIDE, DUE TO ITS RADIOACTIVITY.<sup>1</sup>

BY GEO. B. PEGRAM AND HAROLD W. WEBB.

A BOUT four kilograms of thorium oxide were placed in a spherical Dewar bulb, and this, with a metal cylinder for protection, was put in an ice-bath.

Thermoelements with one set of junctions in the thorium oxide, the other set at the temperature of the ice, showed that the mass of thorium oxide maintained a higher temperature than the ice-bath. Heat was then introduced at a known rate into the mass of thorium oxide, by sending a small current through wires laid in the thorium oxide. Comparing the temperature elevation due to the radioactivity of the thorium oxide alone with the temperature elevation maintained when heat was being introduced at a known rate by the current, the thorium oxide used was found to be liberating heat at the rate of  $.96 \times 10^{-6}$  calories per hour per gram, or about  $\frac{1}{10}$  erg per second per gram. From this value the heat developed by pure thorium oxide in its equilibrium state was calculated to be  $2 \times 10^{-6}$  calories per hour per gram. Measured by the total energy liberated, thorium oxide is then about a three millionth part as radioactive as radium bromide.

## CONTACT ELECTROMOTIVE FORCE AND COHESION.<sup>1</sup>

#### BY FERNANDO SANFORD.

I<sup>N</sup> the consideration of the phenomenon of contact electromotive force in metals the writer has been led to the conclusion that it is definitely related to the specific inductive capacity, so that a metal having a It also seems probable that cohesion, like chemical affinity, is due to electric attractions, and since the electric attraction between two charged bodies is inversely as the specific inductive capacity of the intervening medium, the attractions between the molecules of bodies should vary according to the same law.

The above assumptions lead to the conclusion that the voltaic series should be inversely as the cohesion series.

Lacking direct data on the cohesion of metals, I have attempted to test the above hypothesis by relating the voltaic series to the melting points, the expansion coefficients and the hardness of the metals. The recent valuable work of Professor T. W. Richards and his students on compressibility has given still better data for estimating the cohesion between the molecules of metals. I would accordingly beg leave to submit to the Physical Society the following table, which seems to me to suggest more than an accidental relation between electromotive force and cohesion.

Voltaic Series.	$\underset{\times \text{ 10}^{6}.}{\text{Compressibility}}$	Melting Point.	Expansion Coefficient.	Hardness
Cæsium	61	26.5	:	.2
Rubidium	40	38.5		.3
Potassium	31.5	58		.5
Sodium	15.5	95	.000072	.4
Lithium	8.8	180		.6
Zinc	1.5	419	.000029	2.5
Lead	2.2	330	.000028	1.5
Tin	1.67	230	.000022	1.8
Iron	.38	1,500	.000012	4.5
Silver	.82	950	.000019	2.5-3
Copper	.54	1,054	.000017	2.5-3
Gold	.47	1,035	.000015	2.5–3
Platinum	.21	1,780	.000009	4.3
Carbon	.5	unmelted	.000005	10

As will be seen, iron is the most marked exception in the list. Its other properties would make it seem to belong just above platinum in the voltaic series. It is known that iron may exist in two allotropic conditions, but the temperature of its non-magnetic form is much above that of the measurements under consideration. Its thermo-electric curve also indicates that its position in the voltaic series would be very different at either higher or lower temperatures.

Zinc also seems to be out of place in the series as indicated by all the properties considered except its expansion coefficient. Its other properties would indicate that it belongs between lead or tin and silver in the voltaic series. It may, perhaps, be questioned whether the zinc which has been used in contact electromotive force determinations has been carefully purified.

The data given in the above table has been taken mostly from Landolt and Boernstein's tables except the compressibility, which is taken from Professor Richards's article in Zeit. phys. Chem., LXI., 196, December, 1907.

STANFORD UNIVERSITY, February 14, 1908.

Some Properties of Light of Extremely Short Wave-Length.<sup>1</sup>

#### BY THEODORE LYMAN.

S CHUMANN has investigated the absorption of some gases in the region of the spectrum lying on the more refrangible side of  $\lambda 1,850$ . The present paper is chiefly concerned with a repetition and extension of this work. The writer has employed a vacuum grating spectroscope; the superiority of this instrument for purposes of exact measurement, over the prism apparatus of the earlier investigator, has led to some new and important results. A detailed report of these results will be found in the Astrophysical Journal for March, 1908; they may however be briefly stated as follows:

Oxygen, in thicknesses of I cm., absorbs strongly in the region more refrangible than  $\lambda$  1,850, but contrary to the results obtained by Schumann, the absorption is in the form of a band. Hydrogen, argon and helium in thicknesses of about 1 cm. are transparent. Nitrogen in the same thickness absorbs very slightly. Carbon monoxide and carbon dioxide absorb quite energetically, but their action is unlike that of oxygen, since in place of one broad region of absorption, they give rise to eight or more narrow bands. It appears that the behavior of the air is to be ascribed to the action of the oxygen and nitrogen which it contains. The addition of ozone either to air or to oxygen does not seem to affect the absorption of these gases in the region under consideration. The factors, therefore, which set the limit to the extent of the solar spectrum may be different from those which operate in the region of light more refrangible than  $\lambda$ 2,000. For between  $\lambda_{2,000}$  and  $\lambda_{3,000}$  ozone is known to absorb strongly.

It seems probable that the absorption of oxygen in the region below  $\lambda$  1,850, which so strongly distinguishes it from the other elementary gases. may be ascribed in part to photo-chemical action. It has long

in wave-length below  $\lambda 1,850$ . So pronounced is this effect that the difference in transparency between quartz and fluorite is readily detected by observing the relative discolorations produced in starch-potassium-iodide test paper when the substances under investigation are interposed successively between the paper and the source of light. The great absorption of a layer of air one millimeter thick may also be easily demonstrated by the same simple means.

Although the investigation has been confined to a single gas path about 1 cm. in thickness, the effect of change of pressure on the absorption has been studied. In the case of oxygen increase in pressure produces an unsymmetrical broadening of the band. This fact taken in conjunction with the experiments on the formation of ozone or hydrogen peroxide are interesting in connection with a theory due to Larmor, which connects the unsymmetrical shifting of the limits of an absorption band with the formation of molecular complexes.

The absorption of oxygen for wave-lengths shorter than  $\lambda 1,850$  is a phenomenon of practical importance and one that characterizes the region discovered by Schumann. It is not, however, the only property which renders this little known part of the spectrum interesting. The increase in photo-chemical effect, in photo-electric action and in volume ionization with increase in the period of the exciting light, together with the striking peculiarities of the spectra of various substances in this region, all combine to indicate that the study of vibrations of very high period may be expected to yield results bearing on some of the relations between ether and matter.

JEFFERSON PHYSICAL LABORATORY,

February 28, 1908.

#### THE ORIGIN AND LIFE OF RADIUM.

#### BY BERTRAM B. BOLTWOOD,

A PRELIMINARY notice has already been published (Nature, October 26, November 10, 1907; Am. Jour. Sci., XXIV., p. 370, 1907) of the separation and identification of a new radioactive element which is present in uranium minerals. Further quantities of this element, to which the name "ionium" has been given, have been obtained in the form of a more highly concentrated preparation having an activity about 2,000 times that of an equal weight of pure uranium. With this preparation, which is essentially free from other radioactive substances, mately 2.80 cm. It is probable that the disintegration of ionium is also accompanied by the expulsion of  $\beta$  particles. Experiments on the relative activities of the different radioactive constituents of a uranium mineral indicate that the values are approximately the following, the activity of the uranium being taken as unity:

Element.	Activity.
Uranium,	1.00
Ionium,	0.35
Radium,	0.45
Radium emanation,	0.62
Radium A,	0.54
Radium C,	0.91
Radium F (polonium),	0.49
Actinium products,	0.36
Sum of activities,	4.72

This value for the sum of the activities is in good agreement with the value obtained directly by measurements of uranium minerals which indicate that the minerals are 4.69 times as active as the uranium which they contain.

The relative activities found for the radium and ionium are in good agreement with the relative ranges in air of the  $\alpha$  particles emitted by these elements which are 3.5 cm. and 2.8 cm. respectively.

Experiments on the growth of radium in solutions of ionium, prepared by various methods from definite quantities of minerals containing known amounts of uranium and radium, indicate that the amount of radium produced in one year by the ionium associated with one gram of radium in minerals is approximately  $3.45 \times 10^{-44}$  grams. This gives the time required for a given quantity of radium to be half transformed into other products (the half-value period) as 2,000 years, with the probability that this differs by not more than 100 years from the true period. Details of these experiments will be published shortly.

A STUDY OF ANOMALOUS DISPERSION BY MEANS OF CHANNELED SPECTRA.<sup>1</sup>

#### BY S. R. WILLIAMS.

SOME years ago, a method was described in the PHYSICAL REVIEW for determining the refractive indices of transparent substances by



were first investigated. The concentrations were those used by Bates in studying magnetic rotatory dispersion. Mr. Bates found no anomalous rotatory dispersion in these solutions, and to corroborate his work asked that these solutions be tested for anomalous dispersion since the dispersion formula indicate that a substance having anomalous rotatory dispersion must also show anomalous dispersion. The results of this investigation substantiate Mr. Bates's work.

The concentration of the fuchsin solution was then increased to two, three and four times that of the original solution, and a study made of these solutions. Even at these concentrations no anomalous dispersion was found although the refinement of the method was such that, for a change in index in the fifth place beyond the decimal point, a shift in the bands would occur, visible to the naked eye. This is a sensibility not to be attained by prismatic methods in highly absorbing media.

#### A CURIOUS IONIZATION EFFECT IN A VACUUM TUBE.<sup>1</sup>

#### BY H. A. PERKINS.

THE following curious effect was discovered in the course of some experiments with the electrodeless discharge. A tube about 20 cm. long, and 1 cm. diameter, having electrodes sealed into its two ends was exhausted to what is popularly known as a "white vacuum." This tube was surrounded by a narrow metal ring of a diameter slightly larger than the tube, and the ring was connected to one terminal of a transformer, the other terminal of the transformer being earthed. When the transformer was giving an E.M.F. of 550 volts or over and a frequency of 60 cycles, the tube showed a marked luminescence and a direct current flowed through a galvanometer connected in series with the tube. The terminal of the tube nearest the exciting ring was always positive. The current was very small when the ring was near the end of the tube, but increased rapidly as the ring neared the center. At the center it reversed in direction coming rapidly to another maximum just beyond that point, and then fell rapidly away as the ring neared the far end of the tube.

A battery inserted in series with the tube could greatly increase these currents or reverse them according to the direction of its E.M.F. and this effect as well as the preceding seemed to indicate much greater ionization when the ring was near the center of the tube.

An electrostatic voltmeter connected to the terminals of the tube indicated its largest values when the ring was nearest one end; these values larger voltages were obtained, thus apparently indicating a much feebler ionization in that position.

To account for these phenomena, a theory, depending on the difference of speed of the ions, has been partly worked out, which accounts satisfactorily for the polarity of the tube, and gives an equation roughly approximating to the current curve obtained.

## THE VARIATION OF THE THERMOMAGNETIC EFFECT IN SOFT IRON WITH THE STRENGTH OF THE MAGNETIC FIELD AND WITH THE TEMPERATURE GRADIENT.<sup>1</sup>

#### BY L. L. CAMPBELL.

THE transversal thermomagnetic effect was first determined in the soft iron under a constant gradient of temperature and a varying strength of magnetic field. The temperature gradient was about 18° C. per. cm., and the magnetic field varied from about 6,000 to 12,000 maxwells per cm. The effect increased with, but was not a linear function of, the field strength. The thermomagnetic rotation coefficient Q increased with the field for awhile, and then gradually decreased. For one iron plate, Q had an initial value of 0.00147, a maximum of 0.00150, and a final value of 0.00148. At the higher limit of the field strength, the effect did not seem to approach a saturation value.

The second determination was made under a constant field strength of about 9,000 maxwells, and the temperature gradient varied from  $15^{\circ}$  C. to about  $65^{\circ}$  C. per cm. The effect here also increased with the gradient, but was not a linear function of it. For the same iron plate as mentioned above, Q increased from 0.00146 to 0.00161, and then fell off to 0.00134. At the highest gradient employed, the effect seemed to approach a saturation value.

In the light of the above determinations, it would seem well, in quoting values of the coefficient Q for metals, always to state definitely the field strength and temperature gradient under which the determinations were made.

JRFFERSON PHYSICAL LABORATORY, HARVARD UNIVERSITY.

<sup>1</sup>Abstract of a paper read before the American Physical Society, in New York, Feb-

## THE

# PHYSICAL REVIEW.

## DISTRIBUTED CAPACITY IN RESISTANCE BOXES.

#### BY A. H. TAYLOR AND E. H. WILLIAMS.

THE error introduced into alternating current precision measurements by the distributed capacity of the ordinary non-inductively wound coils of a resistance box is perhaps not generally appreciated. This error was brought particularly to the attention of one of us<sup>1</sup> in the course of some work with the differential A.C. galvanometer, and the evaluation of the distributed capacity in some typical cases was determined upon.

A substitution of the coil in question in one arm of an Anderson bridge, in the place of a coil practically free from inductance and capacity, offered a convenient method of attacking the problem. The equations of this bridge, taking into account residual inductances in all arms, have been given by Rosa and Grover<sup>2</sup> and, as they point out, residual capacities can be taken account of by considering them as equivalent to negative inductances.

The distributed capacity of an ordinary resistance coil is, we think we can safely state, not by any means entirely due to the bifilar winding and the compact space occupied by the coil. However, since these do have their effect, our ideal coils were wound on wooden frames about 12 cm. in diameter and 18 cm. high. The windings were bifilar; in fact they were braided together before wound. Consecutive turns were, however, separated 5 mm. The braiding insured that the coils were absolutely non-inductive, but it

<sup>1</sup> A. Trowbridge and A. H. Taylor, PHYS. REV., December, 1906.

<sup>2</sup> Bulletin of the Bureau of Standards, Vol. I., No. 3.

#### A. H. TAYLOR AND E. H. WILLIAMS, [Vol. XXVI.

seemed possible that there might be some noticeable distributed capacity. In order to determine this, we used two identical 1,000-ohm coils of No. 40 Advance wire, alternately in an arm of the Anderson bridge. One coil was in air, the other in kerosene, which on account of its high dielectric constant, would have increased the capacity of one coil several fold. The balance of the bridge, as determined with a very sensitive A.C. galvanometer,<sup>1</sup> was not notice-ably disturbed on substituting one coil for the other. This means that the distributed capacity of our ideal coils is so small that even when increased several fold it is neglible.

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The equation of the Anderson bridge, as used by Rosa and Grover, is

$$L = cS\left[\frac{r(P+R)}{R} + P\right] + a - \beta,$$

where  $\alpha$  and  $\beta$  are terms involving the residual inductances  $l_1, l_2$ , etc., of the different branches. The term  $\beta$  is so small with any ordinary frequencies that it is entirely negligible. The other term is

$$a = \frac{\mathbf{I}}{R} \left[ l_1 S - l_2 R - l_3 Q + l_4 P \right]$$

The coils tested were alternated with ideal coils in the branch R, so that the portion of  $\alpha$  of interest is

$$\frac{1}{R}[-l_3Q] = -l_3\frac{Q}{R}.$$

If  $l_2$  is due to distributed capacity, considered as in parallel with the branch R;  $l_2 = -R^2C'$  where C' is the value of the distributed capacity. Hence the change in the value of L on substituting a given coil for an ideal coil is  $\Delta L = RQC'$ .

Balance of the bridge was restored by changing r, whose dis-

Box No.	Coil.	Resistance in Ohms.	$\Delta L$ in M.H.	Capacity C M.F.
2894	1,000-ohm.	1,000.5	.517	.000517
2896	1,000 ''	1,000.8	.57	.00057
2897	lst 1,000 "	1,000.7	.59	.00059
"	2d 1,000 "	1,000.9	.57	.00057
2898	lst 1,000 "	1,000.7	.53	.00053
"	2d 1,000 "	1,000.6	.53	.00053
2899	1,000 ''	1,000.8	.59	.00059
2900	1,000 "	1,001.2	.577	.000577
2615	lst 1,000 "	1,000.5	.535	.000535
"	2d 1,000 "	1,000.4	.485	.000485

TABLE I.

Wolff Boxes.

TABLE II.

Leeds and Northrup Coils.

Physics Box No.	Coil,	Resistance in Ohms.	$\Delta L$ in M.H.	Capacity in M.F.
1	1,000-ohm.	1,000.2	.074	.000074
3	1,000 "	1,000.2	.074	.000074
4	1,000 "	1,000.4	.077	.000077
6	1,000 "	1,000.0	.070	.000070

TABLE III.

Wolff Box No.	Coil.	Resistance in Ohms.	$\Delta L$ in M.H.	Capacity in M.F.
2894	1,000-ohm	1,000.5		
2896	1,000 ''	1,000.8	.563	.000281
2894	1,000 ''	1,000.5		
2899	1,000 ''	1,000.9	.552	.000276
2896	1,000 ''	1,000.8		
2899	1,000 ''	1,000.9	.564	.000282
2897	1st 1,000 ''	1,000.7		
"	2d 1,000 "	1,000.9	.563	.000281
2898	1st 1,000 "	1,000.7		
"	2d 1,000 "	1,000.6	.56	.00028
2900	1,000 "	1,001.2		
2898	1st 1,000 "	1,000.7	.586	.000293
2900	1,000 ''	1,001.2		
2898	2d 1,000 "	1,006	.565	.000282
2615	1st 1,000 "	1,000.5		
"	2d 1.000 "	1,000.4	.528	.000264

Two 1,000-ohm Coils in Series.

Table I. gives the results obtained with the 1,000-ohm coils of boxes made by O. H. Wolff, Berlin. These coils are wound on brass, heavily coated with schellac, and baked very hard. Their capacity is relatively very large, and fairly consistent for different coils of the same size.

Table II. gives the values obtained from 1,000-ohm coils made by Leeds and Northrup, wound on wood and coated with shellac. The capacity is about one eighth as much as that of the Wolff coils.

By placing two coils of equal resistance and capacity in series, a resultant capacity of one half that of one coil should be obtained. Table III. shows the result of a series of such determinations, the capacity in this case being nearly one half of the value for single coils.

T	ABLE	I	V.	
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Two 1,000-ohm Coils in Parallel.

Wolff Box No.	Coil.		Resistance in Ohms.	ΔL in M.H.	Capacity in M.F.
2894	<b>1,000</b> -o	hm		•	
2896	1,000	"	500.5	.554	.001108
2897	1st 1,000	"		!	
2898	1st 1,000	«.	500.35	.572	.001144
2899	1,000	"			
2900	1,000	"	500.5	.576	.001152
2898	1st 1,000	"	T		
2899	1,000	"	500.6	.579	.001158
2898	2d 1,000	"			
2899	1,000		500.5	.554	.001108
2897	2d 1,000	"			
2898	1,000	"	500.6	.54	.001080
2896	1,000	"		1	
2900	1,000	"	500.5	.576	.001152

Т	ABLE	V.

Wolff Box No.	Coil.	Resistance in Ohms.	eL in M.H.	Capacity is M.F.
2894	500-ohm	500.7	.084	.000168
2896	500 ''	500.6	.080	.00016
2897	500 ''	500.6	.080	.00016
2898	500 ''	500.6	.108	.000216
2899	500 _ ''	500.6	.080	.00016
2900	500 ''	500.6	.080	.00016

500-ohm Coils Alone.

## TABLE VI.

Wolff Box No.	Coil.	Resistance in Ohms.	aL in M.H.	Capacity in M.F.
2897	500-ohm	500.6	1	
2898	500 ''	500.6	.09	.00009
28 <b>99</b>	500 ''	500.6		
2900	500 ''	500.6	.108	.000108
2897	500 ''	500.6		
2900	500 "	500.6	.091	.000091

#### Two 500-ohm Coils in Series.

## TABLE VII.

## 2,000-ohm Coils Alone.

Wolff Box No.	Coil.	Resistance in Ohms.	a <i>L</i> in M.H.	Capacity in M.F.
2615	2,000-ohm	2,000.6	1.225	.000612
2897	2,000 ''	2,002.5	1.26	.000630
2898	2.000 "	2.001	.818	.000409

## TABLE VIII.

2,000-ohm Coils in Parallel.

Wolff Box No.	Coil.	Resistance in Ohms.	aL in M.H.	Capacity in M.F.
2615	2,000-ohm			
2698	2,000 ''	1,000.4	1.047	.001047
2615	2,000 ''			
2697	2,000 ''	1,000.8	1.273	.001273
2697	2,000 ''			
2698	2,000 "	1,000.9	1.075	.001075

## TABLE IX.

1,000-ohm Coils Alone. Frequency, 114 Cycles.

Wolff Box No.	Coil.	Resistance in Ohms.	aL in M.H.	Capacity in M.F.
2894	1,000-ohm	1,000.5	.487	.000487
2896	1,000 ''	1,000.8	.491	.000491
2897	1st 1,000 "	1,000.7	.509	.000509
2897	2d 1,000 "	1,000.9	.512	.000512
2898	1st 1,000 "	1,000.7	.509	.000509
2898	2d 1,000 ''	1,000.6	.508	.000508
2900	1,000 "	1,001.2	.536	.000536

The distributed capacity of 500-ohm coils was then measured, by substituting them in place of the two ideal 1,000-ohm coils in parallel. These gave values much less than the 1,000-ohm coils, as will be seen from the following table :

TABLE X.

-	_				
Wolff Box No.	I.	Coll.	Resistanc Ohms		Capacity in M.H.
2897		2,000-ohm	2,002.	.5 1.218	.000609
2898	1	2.000 "	2,001	.777	.000388

This shows clearly the advantage of building up a large resistance out of smaller units. Connecting two coils in parallel should double the capacity. This is shown in Table IV. Table V. gives the values for the distributed capacity of Wolff coils of 500 ohms, while Table VI. shows the effect of putting two such coils in series.

Table VII. shows that the capacity of the 2,000-ohm coils is but little larger than that of the 1,000-ohm, which leads to the suspicion that the effect is peculiar to the inner layers of the coils. This was verified later.

Table VIII. shows the effect of paralleling 2,000-ohm coils.

Up to this point all observations had been taken with a 60-cycle A.C. with very prominent third harmonics present in such a way as to give a very peaked wave. As a check on results a frequency of 114 cycles, with a fairly good wave form was now used. Table IX. gives the results for the 1,000-ohm Wolff coils, while Table X. refers to two of the 2,000-ohm coils.

Comparison with Tables I. and VII. shows the capacity as determined at the higher frequency to be uniformly lower.

The negative term  $\beta$  in the equations of Rosa and Grover is not of sufficient magnitude to account for this discrepancy, which is somewhat larger than the probable experimental error.

The problem of immediate interest was then to determine the cause of the high value for the distributed capacity of the Wolff coils.

Two coils were wound, one on a brass and one on a wooden core, otherwise exactly similar. The brass core gave slightly higher



values, but neither coil had a capacity much exceeding that of the Leeds and Northrup coils. The effect of shellac was to cause an enormous increase in capacity, due probably to electrolytic action. This can be obviated by baking the coils at about 120°, in the case of the one with the brass core, for several days, as the layer of schellac next to the brass core crusts over and dries very slowly.

One of the Wolff coils was then soaked in alcohol and baked repeatedly for several days, resulting in an appreciable lowering of the capacity, but leaving it still many times higher than the Leeds coils.

Our 1,000 coil wound on wood, in exactly the same manner as the Wolff coils, was of No. 36 Advance, and had a capacity of .00016 M.F. The Wolff coil was of a larger size wire, apparently No. 34 Manganin. A coil of No. 40 Advance gave a very small negative value for the distributed capacity, i. e., the residual inductance exceeded the capacity. On the other hand, a coil made of No. 34 Advance gave a capacity of .00048 M.F., which compares with the Wolff coil which had been soaked in alcohol and baked (cap. .00045). The conclusions are apparent. In order to increase their ability to carry current, the Wolff coils are made of rather large, and hence long, wire. This large surface gives an abnormal value to the distributed capacity, which is still farther slightly increased by the fact that, in order to facilitate cooling, the coils are wound on brass cores, so that even after days of baking the inner layer of schellac does not dry thoroughly. This also slightly increases the capacity.

While these coils are excellent for D.C. work, it is evident that they possess a serious defect from the standpoint of precise A.C. measurements.

UNIVERSITY OF WISCONSIN, February 24, 1908.



### O. C. CLIFFORD.

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# DETERMINATION OF THE SUSCEPTIBILITY OF COP-PER AND TIN AND THEIR ALLOYS.

#### BY O. C. CLIFFORD.

THIS investigation was begun at the suggestion of Professor Michelson to determine, if possible, what function the magnetic susceptibility of an alloy of copper and tin is of the susceptibility of the constituents. As a result of the investigation a simple relation has been found between the susceptibility of the alloy and its per cent. composition. Furthermore the value of the

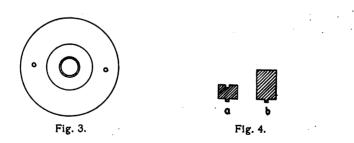


susceptibility of copper and tin have been determined with an accuracy heretofore unattained, and the susceptibility of bismuth has been explored through a range of field strength much lower than that used in preceding investigations.

After spending considerable time in attempting to determine weak susceptibility by ballistic methods, the following torsional balance method was adopted. An electro-magnet, Fig. I, with large bored pole pieces N-S placed vertically and with small poles p, inserted in the face of N and S, was used to produce the magnetic field. To the top of N was attached a tube with an adjustable head through which worked a slotted screw ending in a chuck for holding the torsional fiber attached to the spindle of the system s. a and bgave two horizontal movements for centering the test pieces t with reference to the poles p. c gave a vertical centering. When the clamping screw system which was suspended by a three mil phosphor bronze ribbon. This shaft was lowered into the tube and the taper just below the mirror fitted snugly into the system disk, Fig. 3. The shaft and

disk were made of white celluloid as that material was found very free from iron, strongly diamagnetic and showed any dirt lodging upon it. The fact that it was diamagnetic tended to make it self centering, as the weakest part of the field was in the center of the holes through the large poles. The disk was provided with a collar about which a split inertia ring could be slipped and had two diametrical holes, 4.36 cm. apart, into which the bismuth test pieces, Fig. 4, a, actual size, could be slipped. These test pieces were the same diametér as the test coil used in exploring the field, so they had the same field through them as was measured by the coil. As the method was a repulsion one, the bismuth test pieces were always in place. Fig. 4, b, actual size, shows a test piece of other material, which was placed directly on top of the bismuth.

The current used to excite the field magnet was taken Fig. 2. from storage cells. Connections were made in such a manner with dynamo and slide-wire resistance that the current through the field could be varied from .5 to 2 amperes and sent in either direction through the magnet. For change of



direction a double knife switch was used. Current determinations were all made by means of a Weston ammeter. As the absolute value of the current was not necessary, the ammeter was not calibrated.

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### O. C. CLIFFORD.

### METHOD OF TAKING READINGS.

The bismuth test pieces having been placed in position on the spool, they were raised or lowered by means of the nut on the slotted screw so that they were about midway between the small pole pieces. A lowering or raising of several millimeters caused no change in deflection, showing a fairly vertical field. By means of the two right angled sliding ways and the large milled head with the tangent screw for final adjustment, the pieces were then put in line with the small pole pieces and centered for the magnetic field, so that a movement of a millimeter or two on the circular scale would cause them to swing front or back, when the field was thrown on. In as much as it was impossible to bring the system of relatively large moment of inertia exactly to rest, the zero was taken by the method of oscillations. These were however never greater than one or two per cent. of the total deflection.

# Solution from the Readings.

If V is the volume of one of the test pieces, H the magnetic field strength at the point where equilibrium of forces exists, dH/dxthe rate of change of magnetic field at this point and f the magnitude of the force acting upon the test piece,

$$f = kVH \, dH/dx^{1}$$

k is the susceptibility and dx is taken in the direction of the arc. Solving this equation for k, we get

$$k=\frac{f}{VH\,dH/dx}.$$

### The Determination of f.

To find the value in dynes of the force of restitution, it was first necessary to find the moment of torsion u of the fiber. This was

The force f acting on the test piece is obtained from the relation  $fr/\vartheta = u$ , where r is one half the distance between the test pieces and  $\vartheta$  is the angular deflection in radians. To express  $\vartheta$  in scale readings we have  $\vartheta = d/2R$ , where d is the deflection in cm. on the scale and R is the radius of the scale. Substituting back,

$$f = \frac{u\vartheta}{r} = \frac{ud}{2Rr} = \frac{4\pi^2 Kd}{2Rr(t_2^2 - t_1^2)}$$
$$= \frac{4\pi^2 \times 14.52d}{2 \times 100 \times 2.18(41.44^2 - 27.265^2)} = .001350d.$$

Multiplying the constant, .00135, by the deflection in cm., corrected as will be explained, gave the force of restitution in each case.

# Determination of V.

As the volumes of the test pieces were in some cases not over .05 c.c., this operation had to be very carefully done. After trying various methods the best results were obtained by arranging two pans on an assay balance with the lower one in water at all times and the upper one in the air. These two pans were joined together by a No. 40 wire so as to lessen the action of the surface film. Two weighings were then sufficient. Their difference gave the volume.

# DETERMINATION OF H.

H was found in a series of positions by jerking out a test coil and cutting the lines of force. This was one of the most tedious operations in the whole experiment. Fig. 5 shows the slide used

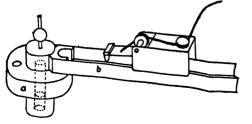


Fig. 5.

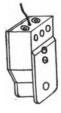


Fig. 6.

a. Attached to b was a mirror in which reflections of the circular scale gave the position and the angular movement. b was provided with a spring for holding the test coil, Fig. 6, in place. The spring could be released and the coil drawn out by suitable rubber bands.

To calibrate the exploration test coil it was connected in series with the galvanometer and another coil placed in the center of a standard solenoid, through which the current could be reversed. Then the equation giving the magnetic flux corresponding to any reading  $\vartheta$  for the test coil is

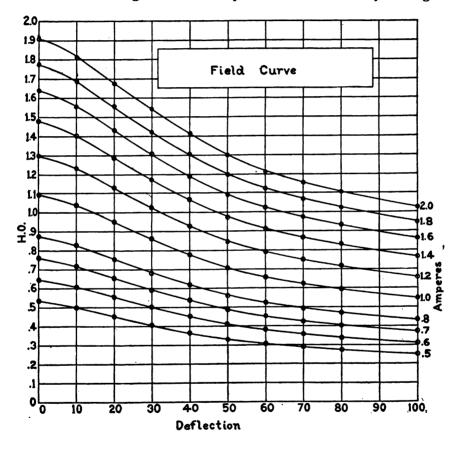
$$H = \frac{4\pi \frac{N_1}{L_1} A_1 n_1 a_1}{5na} \frac{\vartheta}{\vartheta'}$$

where  $N_1/L_1$  are the number of turns per cm. in the standard solenoid;  $n_1$  and  $a_1$  are the number of turns and area of the standard coil placed in the solenoid; n and a are the same for the snatch coil and  $\vartheta'$  is the deflection caused by the reversal of a current of  $A_1$  amperes in the solenoid. The values of these constants were  $N_1/L_1 = 47.3$ ,  $n_1 = 41$  and n = 63 turns,  $\vartheta' = 3.28$  cm.,  $A_1 = .07$  ampere,  $a_1 = 66.4$ and a = .203 square cm. Substituing these values,

The test coil was pushed into b, Fig. 5, and held by the spring. The galvanometer was on another pier so as not to be jarred. The observer after setting the coil went to the galvanometer telescope and by a sudden jerk released the coil and observed the deflection. The coil was again set and released. About 2,000 such observations were made in plotting the field. A series of tests was made on one pair of poles and then on the other pair. It was found that the flux was so nearly the same that there was a variation of not more than four parts in 1,500. So the accurate plotting of the field was all made at one pole. One difficulty that showed itself continually was the residual magnetism in the field-magnet. When these tests as well as the deflections of the test pieces were run, it was almost impossible to do away with all residual magnetism, so as to start from the same condition. It was found that the double knife switch worked better when reversed by hand than any other means. After



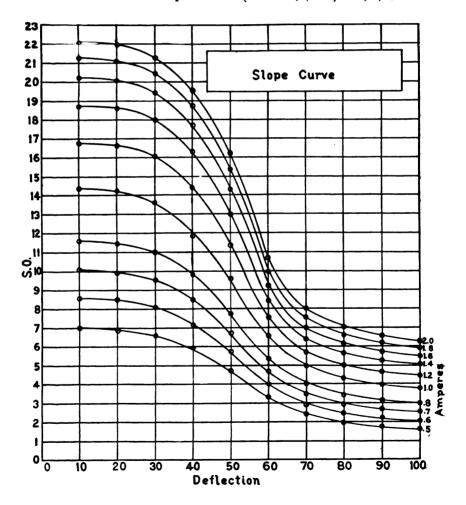
centering the field by means of a piece fitted into Fig. 5, b and around the pole, galvanometer deflections were observed for each tenth radian out to one radian. Here the position was fixed and the current was increased. As a check at .5, I and 2 amperes, the current was kept constant and the coil was moved across the field. These two sets of readings were taken to plot the field curve. By reading



off the ordinate on this curve corresponding to the current used in the magnet and the deflection of the test piece and multiplying by 540, the field strength was found. In the data this ordinate is called H.O.

# DETERMINATION OF dH/dx.

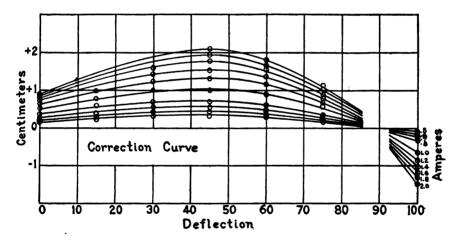
After the field curve was finished the slope at each 10 cm. deflection was found by finding the difference in ordinates in centimeters for two points 40 cm. apart on the axis of abscissas. From this data was drawn the slope curve with difference in ordinates and deflection in centimeters as ordinates and abscissas. To find the slope from this curve one found the ordinate corresponding to the current used and the deflection and multiplied by 15.38, for a motion of 40 cm. on the scale corresponded to  $(2.18 \times 40/100) = 872/1,000$  of



one centimeter motion of the test piece and the scale of the slope curve is forty times that of the field curve. So the slope constant  $= (540 \div \frac{872}{1000})/40 = 15.38$ . These ordinates in the data are called S.O.

# CORRECTION CURVE.

The celluloid of which the spool and spindle was made was diamagnetic as a whole, but in working or otherwise small traces of iron lodged in the material and caused a deflection of the spool alone when the field was thrown on. This made it necessary to observe the deflection from a certain position in the field for each of the fields corresponding to the currents used. From these observations a correction curve was drawn. In the spool used this cor-



rection was such as to subtract from the deflections. The deflection minus the correction, which is marked D.C. in the data, multiplied by the fiber constant, .00135, gave f, the restoring force in dynes.

### RESULTS ON THE SUSCEPTIBILITY OF BISMUTH.

As the method used depended upon the test pieces having their total susceptibility negative, bismuth test pieces were used to make the throw from the central position as large as possible. If the total susceptibility had been positive, they would have been drawn to the center of the field, no matter how weakly positive. The specimen to be tested was placed upon the bismuth. There was an increase

or decrease of deflection as the added specimen was diamagnetic or paramagnetic. As the whole series of experiments depended upon the accuracy with which bismuth was determined, one set of such determinations will be given.

•	Bismuth	N'o.	2.	March	8,	1907
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Amp.	1	1	3	_ 4	Def.	Cor.	D.C.		н.о.	н.	<b>S.O.</b>	8.	-«×10-4
.0	38.6	38.6	38.6	38.6									l
.5	87.8	87.8	87.8	88.0	24.62	.34	24.28						14.0
.6	104.3	103.7	103.8	103.9	32.66	.48	32.18	.0434	.48 <sup>8</sup>	263	7.97	122.4	14.2
.7	115.9	116.0	116.2	116.1	38.72	.60	38.12	.0513	.544	<b>294</b>	8.70	133.6	13.8
.8	126.1	126.3	125.9	126.4	43.74	.75	43.04	.0580	.595	322	9.15	140.6	13.6
1.0	141.9	141.9	142.0	141.7	51.64	1.01	50.63	.0682	.698	377	9.10	140.0	13.6
1.2	153.2	153.0	152.9	153.4	57.26	1.20	56.06	.0758	.803	433	8.40	129.2	14.3
1.4	161.9	162.0	161.8	161.7	61.62	1.32	60.30	.0814	.903	488	7.90	121.6	14.6
1.6	168.9	168.8	168.7	168.7	65.09	1.36	63.73	.0860	.996	538	7.77	119.4	14.1
1.8	174.9	174.8	174.9	174.8	68.12	1.39	66.73	.0900	1.076	580	7.75	119.0	13.8
2.0	180.1	180.1	180.0	180.0	70.72	1.39	69.33	.0937	1.149	620	7.70	118.0	14.0
-	<i>V</i> = .0946 c.c.						Mean $\kappa = -14.03 \pm .33 \times 10^{-6}$ .						

As will be noticed from the H. column, the field strengths where these tests were made varied from 237 to 620 lines. This test gave  $- 14.03 \times 10^{-6}$  for bismuth. Two other tests gave - 13.95 and - 13.82. The mean of these three is  $- 13.92 \pm .08$ .

Van Ettenhausen<sup>1</sup> has made the most exhaustive study of the susceptibility of bismuth and his value found in various ways was about -14.00, though all of his values were in fields of from 2,500 to 8,000 lines instead of from 200 to 600 lines, the range of field strengths used in these determinations. Wills<sup>2</sup> found that for field strengths of from 1,600 to 10,000 lines the susceptibility of bismuth was approximately constant. My work would seem to show for the lower field strengths a constant value also. Wills' value was much too low compared with Van Ettenhausen's. In my preliminary tests it was found that one pair of test pieces was less diamagnetic than another pair cut from the same stick. It was noticed that the less diamagnetic was cut with a dull tool. So both specimens were boiled in hydrochloric acid to remove abrased iron and their values became the same and constant. Wills' low value may have been

<sup>1</sup> Pogg. Ann., clx., p. 1, 1877. <sup>2</sup> Phil. Mag., 5 Series, 45, p. 446.



due to iron contamination of this sort. After it was thus discovered that the iron left on the surface by the abrasion of the tool was sufficient to influence the susceptibility of the specimen to so large a degree, all the test pieces used in these experiments were boiled in hydrochloric acid to remove this iron.

### **RESULTS** ON THE SUSCEPTIBILITY OF TIN.

The first tin used was Kahlbaum c.p. Tests were made of this by cutting out of the square sticks in which the tin came the specimens. This tin from several lots gave about the same value for k, +.5 to  $+.6 \times 10^{-6}$ . One of these specimens was tested without boiling in hydrochloric acid to find the effect of the iron. This sample had a value of  $+3.42 \times 10^{-6}$ , which fell to the same as the others when thoroughly boiled in hydrochloric acid. This Kahlbaum tin which by analysis showed a trace of iron did not seem pure enough to make suitable alloys, so an effort was made to obtain the tin in a purer condition. The general method employed for obtaining pure tin was the same in all the following cases. Tin was dissolved in nitric acid forming metastannic acid, the contaminations remaining in solution as nitrates. The white precipitate was thoroughly washed with distilled water to free it of all nitrates, was dried in a steam bath and was mixed with lamp black and reduced by heating in a gas furnace. Lamp black was chosen as the reducing agent, because it seemed the form of finely divided carbon most likely to be free from iron. Three different crucibles were used in which to make this reduction, fused quartz, fused magnesium oxide and a carbon crucible made by boring out two inch electric furnace carbons and boiling in hydrochloric acid to free from all abrased Specimens obtained from the three were almost exactly alike iron. in susceptibility. So an amount sufficient for these experiments was reduced in a carbon crucible.

The susceptibility of the tin alone was found from that of the sum by taking -13.8 as the susceptibility of the bismuth in the sum and solving according to relative volumes as shown. This gave the tin a susceptibility of  $+.31 \times 10^{-6}$ ; that is, tin was obtained which was slightly paramagnetic and not diamagnetic as Faraday<sup>1</sup> obtained

<sup>1</sup> Faraday's Exp. Researches, Series XXI., 2399.

it in 1845. It seems probable that there may be a slight iron contamination still present. This tin however seemed sufficiently pure for our purposes and was used in making the alloys.

Amp.	I	2	3	4	Def.	Cor.	D.C.	5	<b>H.O</b> .	н.	8.0.	8.	- ××10
.0	38.5	38.5	38.5	38.5									
.5									1				
.6		1		]			ļ						
.7	89.0	89.1	88.4	88.1	25.08	.54	24.54	.0332	.624	337	9.80	150.4	3.20
.8	100.7	100.8	101.3	101.2	31.25	.71	30.54	.0413	.676	365	10.89	167.6	3.30
1.0	117.5	117.2	117.2	117.1	38.38	1.04	37.34	.0504	.791	427	12.49	192.0	3.02
1.2	129.2	129.0	128.9	128.8	45.24	1.32	43.92	.0586	.883	477	13.03	200.0	3.00
1.4	137.8	137.6	137.5	137.4	49.54	1.52	48.02	.0640	.977	527	13.18	203.0	2.95
1.6	144.6	144.2	144.0	144.0	52.85	1.66	51.19	.0683	1.068	576	12.90	198.0	2.93
1.8	149.7	149.7	149.5	149.6	55.56	1.77	53.79	.0717	1.150	620	12.47	192.0	2.95
2.0	154.4	154.4	154.2	154.5	57.95	1.86	56.09	.0750	1.225	660	11.85	182.0	3.07

Tin. May 6, 1907.

Volume Sn = .1563 c.c. " Bi = .0488 " Total = .2051 "  $-13.8 \times 488 + 1563\kappa = -2051 \times 3.05$   $1563\kappa = 6734 - 6256 = 478$  $\kappa = +.31 \times 10^{-4}.$ 

**RESULTS ON THE SUSCEPTIBILITY OF COPPER.** 

An effort to use copper chips obtained from Kahlbaum was made but this copper was entirely unusable. Even when these shavings were boiled in hydrochloric acid and melted in a boiled carbon crucible, the susceptibility was found to be  $+ 9.2 \times 10^{-6}$ . A sample of native copper from the Calumet and Hecla Mine was obtained. This was tested and showed itself feebly diamagnetic. This first specimen was from a small piece. Later much larger homogeneous pieces were obtained and were cut up carefully with a hack saw, filed to remove any lodged quartz and then boiled in hydrochloric acid to free the surface of iron. In this way pieces for testing and for making alloys were obtained.

Our solution gives this conner a suscentibility of  $-1.22 \times 10^{-6}$ 

#### No. 6.] SUSCEPTIBILITY OF COPPER AND TIN.

tain a little iron. Fleming and Dewar used some copper which they found from +7 to  $+28 \times 10^{-6}$ . It appears therefore that this sample of copper is very pure and probably free of iron.

Amp.	I	2	3	4	Def.	Cor.	D.C.	1	н.о.	н.	8.0.	8.	-x×10-
.0	39.1	39.1	39.1	39.1									
.5	74.6	75.4	74.4	74.8	17.85	.29	17.56	.0237	.460	248	6.92	106.2	4.38
.6	90.2	91.8	90.7	91.5	25.98	.44	25.54	.0345	.522	282	8.32	127.6	4.68
.7	102.5	102.9	102.5	102.7	31.78	.58	31.20	.0421	.583	315	94.1	144.4	4.52
.8	111.7	112.4	111.9	112.1	36.46	.74	35.74	.0483	.641	347	10.33	158.0	4.30
1.0	126.2	127.5	126.2	127.2	43.84	1.05	42.79	.0578	.750	405	11.33	174.0	4.00
1.2	137.3	137.6	137.3	137.4	49.15	1.30	47.85	.0647	.851	460	11.70	179.6	3.82
1.4	145.5	146.0	145.7	145.9	53.34	1.51	51.83	.0700	.949	512	11.45	176.0	3.80
1.6	152.2	152.3	152.3	152.2	56.57	1.60	54.97	.0743	1.042	562	10.85	166.6	3.88
1.8	158.2	158.0	157.7	157.7	59.40	1.68	57.73	.0780	1.123	607	10.26	157.6	3.98
2.0	163.0	162.9	162.8	162.5	61.85	1.75	60.10	.0812	1.198	647	9.85	151.2	4.05

Copper. April 12, 1907.

Mean  $\kappa = 4.14 \pm .26 \times 10^{-6}$ .

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RESULTS ON THE SUSCEPTIBILITY OF COPPER AND TIN ALLOYS.

With the copper and tin thus prepared alloys were made by melting the copper in crucibles made from the furnace carbons boiled in hydrochloric acid and washed, and adding the tin. The smaller per cents of tin combine better and so more of the specimens were made with low value in tin. Heycock and Neville<sup>1</sup> have made a very exhaustive study of copper and tin alloys and an effort was made to make the alloys they considered atomic combinations. Seven alloys were prepared and their susceptibilities determined. Some of them were soft enough to be turned up. Others had to be ground. All were treated with hydrochloric acid before testing. As an example of such a test take specimen No. 5.

The other samples were tested in the same way. The per cent. of copper and tin by mass was found by analysis, because the samples were not all of them homogeneous and some of them had an excess of tin floating on the alloyed part. The per cents by mass

<sup>1</sup> Phil. Trans. of Royal Society, 202 A.

Volume Cu = .1568 c.c. $-13.8 \times 488 + 1568\kappa = -4.14 \times 2056$ "Bi = .0488 " $1568\kappa = 6734 - 8512 = -1878$ Total = .2056 " $\kappa = -1.22 \times 10^{-6}$ 

were changed to per cents by volume, as susceptibility is a function of volume and not of mass.

Amp.	<u> </u>		3	4	Def.	Cor.	D.C.	<u> </u>	н.о.	н.	8.0.	8.	«×10
.0	38.0	38.0	38.0	38.0	:			1	l i			1	
.5					'			i	Í		[	4	!
.6	85.0	85.4	85.7	85.8	23.79	.43	23.36	.0315	.533	288	8.40	129.0	7.50
.7	98.2	99.4	98.9	98.8	30.40	.58	29.82	.0403	.591	319	9.51	146.0	7.66
.8	108.3	108.7	108.8	108.8	35.33	.73	34.60	.0467	.649	350	10.47	160.6	7.34
1.0	124.4	123.9	123.8	123.8	42.99	1.06	41.93	.0567	.756	408	11.52	176.5	6.96
1.2	135.1	135.1	135.0	135.2	48.55	1.30	47.25	.0638	.855	462	11.90	182.6	6.68
1.4	143.6	143.4	143.8	143.9	52.84	1.48	51.36	.0694	.952	513	11.70	179.8	6.68
1.6	150.3	150.1	150.2	150.2	56.10	1.61	54.49	.0736	1.045	563	11.10	170.0	6.78
1.8	155.9	155.8	155.7	155.9	58.91	1.70	57.21	.0772	1.126	608	10.50	161.6	6.97
2.0	160.6	160.7	160.7	160.6	61.33	1.77	59.56	.0803	1.201	649	10.05	152.0	7.20

Cu-Sn Alloy No. 5. May 13, 1907.

Volume Alloy = .0646 c.c. "Bi = .0488 " Total = .1134 "

 $-13.8 \times 488 + 646\kappa = -7.11 \times 1134$ 646  $\kappa = 6734 - 8063 = -1329$  $\kappa = -2.06 \times 10^{-6}.$ 

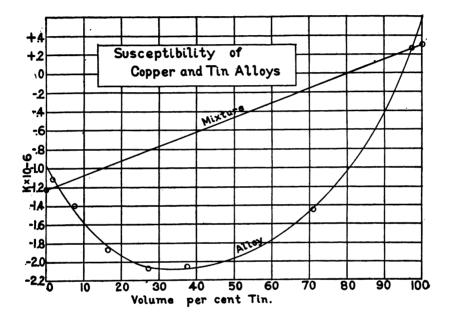
No.	Mass # Sn.	Mass ≶ Cu.	$ \begin{array}{l} M \neq + D \\ = V_{\text{Sn.}} \end{array} $	$  M \neq + D                               $	Vol. Sum.	Vol. ≰ 8n.	K×10 <sup>−4</sup>
1	1.0	99.0	.14	11.16	11.30	1.22	- 1.13
2	7.0	93.0	.96	10.45	11.41	8.41	- 1.40
3	13.8	86.2	1.89	9.68	11.57	16.36	- 1.88
4	24.2	75.8	3.32	8.51	11.83	28.00	- 2.07
5	33.2	66.8	4.55	7.50	12.05	37.8	- 2.06
6	66.4	33.6	9.10	3.77	12.87	70.7	- 1.43
7	97.9	2.1	13.40	.24	13.64	98.0	+ .28

Alloy Results.

The line marked "alloys" on the alloy curve is plotted from the data. The line marked "mixtures" gives the susceptibility on the assumption that this is a function of the per cents by volume. It will be noticed that when the alloys are formed there results a marked increase in their diamagnetism over that of the mixtures. The maximum value on this curve seems to be at about the alloy called speculum metal. Speculum metal is given by Heycock and Neville as one of the atomic compounds of copper and tin. An attempt was made to see whether the resulting susceptibility was

#### No. 6.] SUSCEPTIBILITY OF COPPER AND TIN.

due to per cents of this compound dissolved in an excess of copper or tin. There seemed to be no connection. Probably all three copper and tin compounds are present and influence the results. It will be noticed from the curve that even with these carefully prepared crucibles there was some contamination and change in the susceptibility of both the copper and the tin by remelting.



Heusler<sup>1</sup> has found that a mixture of tin and manganese form an alloy which is much stronger paramagnetically than the manganese alone. The question presents itself, whether the tin increases the diamagnetism of the copper in the same way. Sufficient work has not been done to justify any assumption as to the cause; but all guesses applied to Heusler's alloy seem applicable. These guesses reduce to assuming that some molecular combination has taken place between the metals in the alloy, so that the new compound has new properties, among these new properties a new susceptibility.

The limitations of the apparatus were such that the tests were carried on in a very small range of magnetic field. By designing a

<sup>1</sup> Verhandlung der Phys. Gesell., 5, p. 219, 1903.

special magnet, the range can be much increased and the whole apparatus be made much more sensitive. The experimenter has in mind the making of special apparatus and further work among the diamagnetic metals, with a view to seeing whether some of them may not be made strongly diamagnetic by alloying as manganese is made strongly paramagnetic.

### SUMMARY OF RESULTS.

1. The susceptibility of bismuth as previously found for large field strengths is shown to hold for comparatively low fields.

2. The absolute susceptibility  $+ .31 \times 10^{-6}$  found for a comparatively pure sample of tin.

3. The absolute susceptibility  $-1.22 \times 10^{-6}$  found for a sample of native copper, probably free from iron.

4. The susceptibility of the alloys of copper and tin found to be a function which is not linear but increases with increasing per cent. of tin to a maximum and then decreases.

My thanks are due especially to Professor Michelson who set the problem and who has given valuable suggestions along the way, and also to the other members of the Laboratory Staff who have at all times freely given their encouragement.

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Ryerson Laboratory,
May 31, 1907.
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# GENERAL LAW FOR VAPOR PRESSURES. PART III. VAPOR PRESSURE OF CO.

BY SANFORD A. MOSS.

THE general law for vapor pressures discussed in the previous articles<sup>1</sup> is here applied to observations of vapor pressure of solid and liquid  $CO_2$  due to John Zeleny and Anthony Zeleny<sup>2</sup> and to John Zeleny and Roy H. Smith.<sup>3</sup> Remarkable agreement is found, both for solid and liquid vapor pressures. On the basis of such result, and by use of the Roche law given by Regnault as "Formula K" for water-vapor pressure, saturation-pressure equations are deduced. These represent the observations with reasonable accuracy throughout entire observed range for pressures of from about 1 mm. of mercury for vapor of solid, through the triple point, to critical pressure of 55,000 mm.

In the previous articles it is shown that the absolute saturation temperatures  $T_a$  and  $T_b$  for two given substances at the same vapor pressure, are connected by the relation

$$\frac{\mathbf{I}}{T_b} = c \frac{\mathbf{I}}{T_a} + k \tag{1}$$

where c and k are constants for each pair of substances, for all vapor pressures. It was stated that the law includes a votalizing solid as well as a vaporizing liquid. The present article gives a good example of this.

The law is an empirical one, but it so well represents experiments on varied substances through a wide range that discovery of the rational law in the matter can only result in addition of very small corrections.

We may take the substance a of equation (1) as water vapor,

<sup>1</sup> PHYSICAL REVIEW, Vol. 16, 1903, p. 356; Vol. 25, 1907, p. 453.

<sup>2</sup> Physical Review, Vol. 23, 1906, p. 308.

<sup>8</sup> PHYSICAL REVIEW, Vol. 24, 1907, p. 42.

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whose saturation temperatures are known. Then we have  $1/T_a$  as a known function of the vapor pressure corresponding to the saturation temperature  $T_b$  for the substance b, since it is given by the temperature of water vapor for that pressure. By using this function  $1/T_a$  of the vapor pressure of the substance b, and the function  $1/T_b$  of the saturation temperature  $T_b$ , instead of the actual vapor pressure and saturation temperature, the curve between the two becomes a straight line. That is to say, the ordinates and abscissæ of the usual vapor-pressure curve are so transformed that it becomes a straight line.

Instead of finding values of  $I/T_a$  corresponding to various pressures from a table of water-vapor pressures, we may compute them by a formula. It is shown in the last article that Regnault's "Formula K" (of a form originally due to Roche) gives values for water-vapor pressure which coincide well with the averages of values due to various observers. The values do not coincide exactly with those of Regnault or any one other observer, but do coincide as closely as do the values of various observers. In the preceding article is given the expression for water-vapor pressure (exactly equivalent to the original "Formula K").

$$\log_{10} p = 45.8372 - 1/(0.0264052 - 1.16589/T)$$

Here p is vapor pressure in millimeters of mercury and T is absolute centigrade saturation temperature. It follows that the value of  $1/T_a$ corresponding to a given water-vapor pressure p is a linear function of  $1/(45.8372 - \log_{10} p)$ . As stated, this is by virtue of use of Regnault's "Formula K" for values of water-vapor pressure. From this and the general law for vapor pressures (1), it follows that  $1/T_b$ is a linear function of  $1/(45.8372 - \log_{10} p)$  where  $T_b$  is absolute centigrade saturation temperature and p is corresponding vapor pressure in millimeters of mercury for any substance. As previously expressed, by using 1/T instead of T and  $1/(45.8372 - \log p)$ instead of p, the vapor-pressure curve is made into a straight line.

CO VADOD PRECEIDE ORCEDUATIONS

cover vapor pressure of solid from about 1 mm. of mercury pressure at 140° absolute centigrade temperature, to the triple point at about 218° Abs.; as well as vapor pressure of liquid from supercooled state at about 207° Abs., through the triple point, almost to 0° C., and about 26,000 mm. pressure. The observations agree very closely with those of other accurate observers. So far as the writer knows, they are the only published set of observations making a distinction between curve for liquid and curve for solid vapor pressure, and showing the proper type of discontinuous intersection at the triple point. It is common to assume in this and other cases, that solid and liquid vapor pressures lie on the same smooth curve. This is probably never true however.

The papers cited cover two series of observations. The later and most accurate series covers the entire range above given. The earlier series covers only a portion of the range for solid only and agrees well with the later series. It was published as "Temperatures of CO, Snow at Different Pressures." This is of course equivalent to vapor pressure of solid CO<sub>2</sub>. Many of the observations of the latter series are for mixtures of CO<sub>2</sub> snow with ether and alcohol, which the experiments show to give values identical with the CO<sub>2</sub> alone when stationary conditions are reached. This is as it should be since vapor pressures of ether and alcohol are negligible compared with those of CO<sub>2</sub> at the same temperature. The observed vapor pressure of such a mixture is probably the sum of the vapor pressures of the two constituents. A glance at a curve sheet containing vapor pressures of CO<sub>2</sub>, ether, and alcohol on the same scale, such as the general curve in the first of the preceding articles <sup>1</sup> shows the insignificant values of vapor pressures of latter substances. For instance, at the critical temperature of CO., 31° C., where the vapor pressure is 55,000 mm. Hg, the vapor pressure of ether is about 600 mm. Hg and of alcohol is about 80 mm. Hg. The differences are more marked at lower temperatures which are the present concern. At the triple point of CO<sub>2</sub>, 218° Abs. C., where the vapor pressure is about 4,000 mm. Hg, the vapor pressure of ether is about 7 mm. Hg, and of alcohol some unknown amount very much less. At the lower temperatures where the observations of

<sup>1</sup> PHYSICAL REVIEW, Vol. 16, 1903, p. 357.

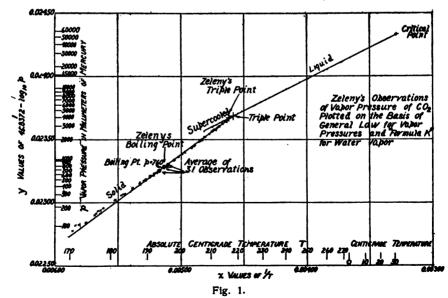
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the mixtures were taken, 156° to 196° Abs. C., the differences are much greater.

The published tables of the  $CO_2$  vapor pressures in the articles under discussion, were smoothed by drawing an arbitrary smooth curve, and therefore were not desirable for an investigation such as the present. Professor John Zeleny very kindly furnished the writer with the original unsmoothed observations, which are wholly used in the following work. Both series of observations are used, no distinction being noticeable.

#### **REDUCTION OF OBSERVATIONS.**

The original observations of the experiments alluded to consisted of corresponding values of centigrade saturation temperature and vapor pressure as height of a column of mercury, for about 150 points for solid, liquid and supercooled liquid  $CO_2$ . For each of these points, absolute centigrade temperature, T (taking 273° Abs.



### No. 6.] GENERAL LAW FOR VAPOR PRESSURES.

duced from the original. Straight lines represented the results with great accuracy. They were drawn by estimation. (In other cases which warrant the labor the method of least squares could of course be used.) Some observed points down to 146° Abs. with very low vapor pressures were given and were plotted, but are not shown on the figure. These were somewhat scattered and were given no weight. For the most part they were above the prolongation of the selected line. The observations in question did not extend to the critical point, so that this was taken as selected by Travers<sup>1</sup> from various observers,  $T = 304^\circ$ , p = 55,000 mm. This point fell exactly on the line previously selected.

### CO<sub>2</sub> VAPOR PRESSURE EQUATIONS.

Two points were taken on each of the lines, solid and liquid respectively, and from them the equations of the lines were computed. For a low pressure of solid, a point on the line is x = 0.005750, y = 0.022835. The triple point is on lines of both liquid and solid and is given by the intersection as x = 0.004583, y = 0.023687. The critical point values were computed from the temperature and pressure above given, yielding x = 0.003289, y = 0.024333. These points give as the laws for liquid and solid respectively

$$0.025975 - 0.4992x = y, 0.027033 - 0.7300x = y.$$

Hence the relations between absolute centigrade saturation temperature T and vapor pressure in millimeters of mercury p for liquid and solid CO<sub>v</sub> are respectively

$$\log_{10} p = 45.8372 - 1/(0.025975 - 0.4992/T),$$
  

$$\log_{10} p = 45.8372 - 1/(0.027033 - 0.7300/T).$$
(2)

A few computed values are given in the table below.

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# SANFORD A. MOSS.

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### Accuracy of Vapor Pressure Equations.

The following table gives a few values computed from the above equations, of course equivalent to values given by the straight lines of the figure. There are also given for comparison figures from the smoothed table of the original paper, headed "Z. and S.," as well as some of the values of Kuenen and Robson<sup>1</sup> and Du Bois and Wills<sup>2</sup> cited in the same paper. In comparisons such as this it must be remembered that very slight differences of temperature make marked differences of pressure particularly with the lower pressures.

Centigrad	le Temp.	Pres	sure, mm. of N	lercury.	
	Abs.	Computed	Smoothed V serva	alues from Ob- tions.	Remarks.
		from eq. (2).	Z. & S.	D. B. & W. and K. & R.	
-150	123	0.028	_	_	Solid.
-134	139	0.85	1.0	_	
-130	143	1.70	2.5	- 1	"
-124	149	4.53	8.0	5.0	"
-112	161	24.5	34.0	40.0	"
-102 ·	171	80.6	99.0	110	
- 85	188	437	435	510	"
- 80	193	671	657		.1
- 78.5	194.5	760	_	_	Normal boiling
					point.
- 70	203	1,472	1,440	1,430	Solid.
- 60	213	2,961	2,980	3,020	"
- 54.8	218.2	4,169	-	_	Triple point.
- 65.5	207.5	2,562	2,508	-	Supercooled liquid.
- 60	213	3,311	3,306	3,270	• • •
- 58	215	3,610	3,610	-	**
- 56	217	3,952	3,945	-	
- 50	223	5,096	5,115	5,020	Liquid.
- 40	233	7,530	7,510	7,460	
- 30	243	10,740	10,800	10,600	

CO, VAPOR PRESSURE.

Inspection of this table and of the points of the figure, shows very close coincidence between smoothed observations and values from equation, except for low pressures of the solid, below about 100 mm. Hg, and for pressures of solid immediately adjacent to and at the triple point. The latter point is discussed later. For low pressures of solid, the equation gives lower pressures than the smooth values selected by Zeleny. However, the observed points are somewhat discordant, so that possibly the smoothed values are not the true Either the general law for vapor pressures fails for low presones. sures of solid, yielding values which are lower than the true ones; or else the difficulty of the observations for low pressures of solid makes them so discordant that it is not possible to select the true values from them. It does not seem possible to reach a positive statement in this matter from present data.

For all pressures of solid above about 100 mm. Hg (except solid pressures close to triple point alluded to later), and for all pressures of supercooled liquid and liquid up to critical point, the equations represent the observations as accurately as is possible with any smooth curve. The smooth curves selected by Zeleny from a plot of direct observations of pressure and temperature, interlace with the curves of the equations, being slightly lower or higher irregularly. In any smoothing of observations there is always some uncertainty, and the smooth values given by the equations are probably as reputable as any other selection.

The fact that the equations represent the observations with such accuracy, that is, the fact that straight lines represent the reduced observations, as shown by the figure, gives a remarkable confirmation of the vapor-pressure laws under discussion. As already stated the coincidence is so close that the empirical laws given must certainly be very close to the unknown exact laws. If a rational law is ever discovered it can only make small corrections in the values given by the empirical laws.

TRIPLE POINT.

exactly on the curve for supercooled liquid, being at  $T = 216.6^{\circ}$  Abs. and p = 3,911 mm. Hg. There is a sudden change in the observed curve for vapor pressure of solid, just below the triple point. The curvature changes rapidly so that the observed vapor-pressure curve seems to bend sharply upward. In the figure it leaves the straight line previously representing the reduced observations, so as to meet the line for liquid at a lower point than the intersection with the prolongation of the straight line for the solid.

Professor Zeleny has suggested to the writer that in this region just prior to melting, "the crystals or other molecular aggregates of the  $CO_2$  gradually break up, the vapor pressure being affected by such a change."

It is to be remarked that the triple point is not the mere "melting point," but the lower extremity of the curve giving melting temperatures for various pressures. Possibly the determination of the point of intersection of this curve with the saturation curves would be of interest in the matter. The observed triple point here alluded to was found by increasing temperature of solid CO<sub>2</sub> exposed to its own vapor, until a point was reached where further addition of heat caused no change of temperature. Does this necessarily give a definite triple point independent of local circumstances?

It may be mentioned that the method of this paper could be applied to observations of vapor pressure of water and acetic acid published in 1884, by Ramsay and Young.<sup>1</sup>

The chart of the first one of these articles<sup>2</sup> gave a line for CO<sub>2</sub> vapor-pressure from Cailletet's observations as reported by Travers.<sup>3</sup>

These seem to be affected by the assumption that solid and liquid vapor-pressure curves are continuous, or else it was unknown that the lower observations are for the solid state. The line given should be replaced by the ones of the present figure.

Note on Parts I. and II. - As remarked in the second of the

form used by the writer. Hence these tables differ slightly from results which would have been obtained from the symmetrical form of the law. This explains the fact, noted in the first of the preceding articles,<sup>1</sup> and not understood at the time, that the points from the tables of "Study of Gases" did not quite lay on straight lines in the large chart of the first article. Such lines therefore may differ slightly from positions exactly corresponding to original observations.

Erratum, Vol. 16, 1903, p. 358, line 5 from bottom : -1/Tshould be  $-1/T_{w}$ .

WEST LYNN, MASS.

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<sup>1</sup> PHYSICAL REVIEW, Vol. 16, 1903, p. 360.

# THE INFLUENCE OF HUMIDITY UPON THE ELEC-TRICAL DISCHARGE FROM POINTS IN AIR.

#### BY JOHN ZELENY.

THE electrical discharge from points in air is affected by the amount of water vapor present. It is of some importance to establish the magnitude of this effect so that the results of experiments performed on different days in the open air may be directly compared, and so that laboratory results for dry air may be applied to such cases, for example, as the discharge from the points of lightning conductors or the discharge from high potential wires.

Tamm<sup>1</sup> experimented on the current flowing from a point in air of various degrees of humidity, but unfortunately his values are given in arbitrary units and were obtained with a single potential of 6,000 volts throughout the series. The results are not suited for reducing observations from one humidity to another because the ratio of the currents for any two humidities may depend upon the magnitude of the currents in question, and upon how the humidity affects the potential required to start a discharge.

The experiments to be described in this paper had for their object the determination of the influence of humidity upon both the voltage required to start a discharge, and the magnitude of the potentials required to produce different currents.

The arrangement of the apparatus was essentially the same as that which was used in some previous experiments on point discharge, and is described on page 306 of Volume XXV. of the PHYSICAL REVIEW. A brass wire 0.26 mm. in diameter and 4 cm. long was used for the discharge point, and its rounded end was No. 6.] THE INFLUENCE OF HUMIDITY.

nometer and a telephone, while the point could be maintained at any desired potential by means of a small Wimshurst machine.

Air was drawn at a uniform rate through the enclosing vessel during each experiment, while the starting potential and the currents for a series of voltages were observed. Fairly dry air was obtained by passing the air of the room through a large calcium chloride tower; moist air was obtained by bubbling air first through hot water and then through water at the room temperature; and air of intermediate degrees of humidity was obtained by using the air of the room directly or after it had passed within different distances from water contained in bottles.

After going through the vessel containing the point and plane, the air passed through two U-tubes containing fresh calcium chloride, and then through a calibrated gasmeter. The water contents of the volume of air measured by the gasmeter was thus obtained from the increased weights of the calcium chloride tubes.

Over twenty experiments were carried out for both the positive and the negative discharges in air of different humidities. The results were all reduced to a common pressure of 74 cm. and a common temperature of  $22^{\circ}$  C. by the method given in a previous paper,<sup>1</sup> and the currents corresponding to the different potentials were then plotted for each case. From these potential-current curves, the values of the potentials were then read which were required to produce certain fixed currents with the air at the different humidities which had been used. Finally, the values thus obtained were plotted to show graphically how the potential required to start a current and that required to produce the currents stated, varies with the humidity of the air.

Fig. I represents these curves for the positive discharge. The ordinates give the potentials required to produce the currents stated, while the abscissæ are expressed in terms of the number of grams of water contained in a cubic meter of air. The abscissæ are expressed in the units given because it has been found that the changes in the point discharge in air which are produced by the addition of water vapor are related to the absolute water content of the air, and not to its relative humidity.

<sup>1</sup> J. Zeleny, PHYS. REV., XXV., pp. 326-331, 1907.

Evidence on this point was first obtained from the readings taken at the different temperatures on different days, but a more thorough test was made by reducing the temperature of the room to  $3^{\circ}$  C. and taking sets of readings for both discharges, first with the air dry

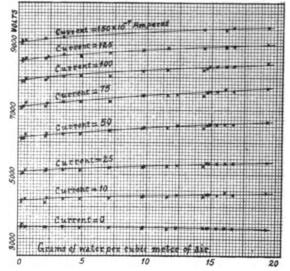


Fig. 1. The influence of humidity upon the positive discharge in air.

and then with the air saturated with water vapor. At this low temperature the saturated air contained only about one third as much water as was present in the saturated air used in the other experiments where the temperature averaged about 22° C.

The results showed that the ratio of the potential required to maintain a given current in saturated air to that required for dry air was much smaller when the air was at this low temperature than when it was at the ordinary room temperature. Moreover this ratio for the cold air corresponded in both discharges to that obtained for warm air of an equal water content, showing that the effect under consideration is dependent upon the absolute amount of water present in the air rather than upon its relative humidity.

As far as any influence of water vapor upon the ions of the air is concerned here, the result might have been expected, for although it has been shown<sup>1</sup> that the presence of water vapor does change

<sup>1</sup> J. Zeleny, Lond. Phil. Trans., 195, p. 231, 1900.



ionic velocities, still this action cannot be related to ordinary condensation at the dew point for C. T. R. Wilson<sup>1</sup> found that drops do not form upon the ions until the air is supersaturated over fourfold.

The points in Fig. I which are marked by circles are those where a faint sound was heard in the telephone indicating that the current was intermittent, at least in part. The readings were discontinued when the sound in the telephone became loud, as it usually did for high values of the current.

The curve for current = 0 in Fig. 1 represents the potentials required to start the current in the different cases. It is seen that the amount of water vapor present has but little effect upon this quantity, although the potential appears to diminish slightly as the amount of water vapor increases, the total change being about one and one half per cent. for the whole range.

The potential required to maintain a given current (between  $10^{-6}$  and  $15 \times 10^{-6}$  amperes) increases with the humidity of the air, as is indicated by the upper curves of the figure. The increase is somewhat more rapid for the drier air, it is relatively not much different for the currents given, and the total change in potential for the whole range from dry to moist air is about seven per cent. in each case.

The ratio of the potentials required to produce a given current in air containing two different amounts of water vapor may be obtained readily from the curves in the figure, and used to reduce other results from the one humidity to the other.

It is desirable for some purposes to know how much the current obtained with some given potential changes with a change in the amount of water vapor in the air. This relation may be obtained by plotting the potential current curves for any two humidities in question, with values taken from the curves in Fig. 1. From these new curves the ratio of the currents for any potential is readily obtained. This ratio varies considerably from one potential to another, and for a given change of humidity is larger than the corresponding ratio of the potentials required to maintain a given current.

<sup>1</sup>C. T. R. Wilson, Lond. Phil. Trans., 189, p. 301, 1897.

#### JOHN ZELENY.

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The results of the experiments on the negative discharge are shown in Fig. 2.

As is usual, the results for the negative discharge are less regular than those for the positive discharge. It was found, however, that this irregularity diminished as the humidity of the air increased,

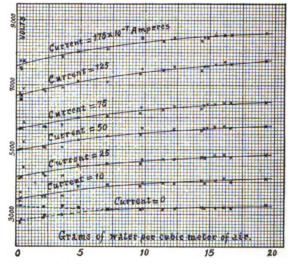


Fig. 2. The influence of humidity upon the negative discharge in air.

which indicates that moist air is to be preferred for experiments on the negative discharge.

The irregularity showed itself markedly in the retardation of the starting potential. As the potential was gradually increased when the air contained but little water vapor, the current would not increase gradually from zero value, but would start suddenly with a considerable magnitude, and it would do this in spite of the presence outside of the vessel of a tube of radium bromide which usually tends to

the average observed values, all of which are not marked. The lower branch represents values of the potentials which were obtained by extending the potential-current curves for these cases downward until they reached the axis for current = 0. Presumably these are the values of the potentials at which the current would have begun to flow had it started to flow gradually. The points on these two branches are not as concordant as would appear from the figure since some of those diverging most from the average have been omitted to avoid confusion.

As seen from the curves in Fig. 2, the potential required to produce a given current increases here also as the amount of water vapor in the air increases, the change being again more rapid when the amount of water present is small. The total increase from dry air to saturated air averages about sixteen per cent. This number does not differ greatly for the different currents used, and is much larger here than it was for the positive discharge.

The curves given may be used for reducing results on point discharge from one humidity to another in the same way as was indicated for the positive discharge.

Some experiments were carried out with alterations in what appear to be the essential experimental conditions, to determine how extended the application of the results here obtained may be. In the first of these, the distance between the point and the plate was changed from 1.5 to 3 cm., and readings were taken for both the positive and the negative discharges in air containing two widely different amounts of water vapor. In the second, similar sets of readings were taken when the point previously used (0.26 mm. in diameter) was replaced by a new one consisting of a brass wire having a diameter of 0.084 mm.

In both cases, the results for both of the discharges agreed well with those here recorded, the widest difference of about one per cent. being well within the experimental errors.

Physical Laboratory, University of Minnesòta, February 24, 1908.

# STUDIES IN THERMO-LUMINESCENCE.

II. VARIATIONS IN THE DECAY OF PHOSPHORESCENCE IN BAL-MAIN'S PAINT PRODUCED BY HEATING.

#### BY C. A. PIERCE.

IN an earlier paper,<sup>1</sup> on thermo-luminescence of Sidot blende, mention was made of the interesting character of corresponding curves for Balmain's paint. These curves were obtained with the apparatus used for the study of Sidot blende. A mercury lamp was used to excite the calcium sulphide, which was in powder form. Since the lamp was made of ordinary glass and the light from it was reflected at a mirror before reaching the powder, the excitation was due to the visible spectrum in the mercury arc. Before each excitation the powder was exposed to infra-red rays in an attempt to bring it to a standard condition.

The action of infra-red rays upon the phosphorescence of calcium sulphide is not so strong as their action upon the phosphorescence of Sidot blende. In the latter case, phosphorescence due to a very long excitation can be killed off almost immediately by infra-red rays and only the highest allowable temperature, just under dull red heat, is able to produce thermo-luminescence without renewed excitation. In the case of calcium sulphide a very long exposure to infra-red rays was necessary to kill off the phosphorescence, and no exposure was found to be long enough to suppress the thermo-luminescence completely. At the beginning of the experiments on calcium sulphide this fact was not recognized. If it had been, the powder could have been brought to an approximately standard condition by heating to a temperature a little higher than the highest temperature at which thermo-luminescence was to be studied. Fortunately, in every case the powder was exposed for one minute to infra-red rays of constant strength, hence it was always brought to a semi-standard condition. No extended attempt

<sup>1</sup>PHYSICAL REVIEW, Vol. XXVI., No. 4, April, 1908.

was made to compare the two methods, since the blue phosphorescence of calcium sulphide is a difficult color to measure in the photometer.

The fluorescence spectrum of this sample of calcium sulphide is shown in Fig. 23. This curve was obtained by comparison with the

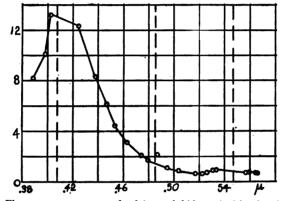


Fig. 23. Fluorescence spectrum of calcium sulphide excited by the visible spectrum of a mercury arc.

light reflected from the surface of a block of magnesium carbonate illuminated by an acetylene flame. Two bands are indicated by the curve, one with a maximum at about  $0.41 \mu$  and the other with a maximum at about  $0.54 \mu$ . The dotted vertical lines show the wave-lengths of the lines of the mercury arc. While the figure indicates a continuous spectrum this is probably due to an error caused by stray light in the spectrophotometer. The effect of this error is twofold; to lower the zero line with respect to the curve and to unduly exaggerate the ratio of the maximum of the band at  $0.41 \mu$  to the maximum of the band at  $0.54 \mu$ . Notwithstanding this correction, the band in the blue is much more intense than the other. This fact was shown by the apparent color of the initial phosphorescence, which was blue.

The effect upon the decay curve of varying the length of excitation is shown in Fig. 24. These surves are plotted with distances of the bending is concentrated in the first part of the curves. These curves are similar to those obtained with Sidot blende, except that the phosphorescence lasts much longer. Hence it is possible to get points relatively nearer the origin. This fact allows one to make a tentative deduction regarding initial intensity and length of excitation at room temperature. A study of Fig. 24 indicates strongly that the initial intensity is greater the longer the excitation, which is the impression obtained when getting the curves. Though it is impossible, with this apparatus, to get a measurement much nearer

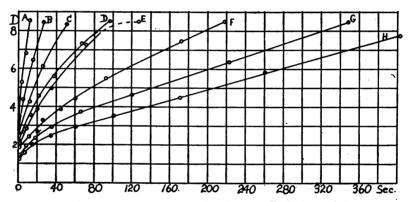


Fig. 24. Effect of varying the length of excitation. Excitation and decay at room - temperature.

Curve	: A,	excited	14.4	sec.	Curve	Ε,	excited	59.9	sec.
"	В,	**	30.1	44	**	F,	**	150.3	""
"	С,	**	30.1	"	"	G,	44	300.0	**
"	D,	"	60.2	"	**	Η,	"	600.0	**

Curves A, B, D and F were taken on the second day and the remainder on the first day of the run.

the origin than 0.8 of a second, yet the eye is sensible to part of the change of intensity before this, giving one a means of estimating roughly the amount of change before the first measured point. The saturation effect is prominent as was the case with Sidot blende.



that the infra-red exposure does not reduce the powder to a standard condition. Curves D and E agree more closely than B and C. A curve, not shown in the figure, excited for 300 seconds, coincides with G. This coincidence may have been due to chance, but it is what would be expected, because the effect of previous history becomes of less importance as the length of excitation is increased.

That the lack of agreement of curves B and C is due to the previous history of the powder is substantiated by the fact that curve Awas observed immediately before curve B, while curve G was gotten immediately before curve C. No deductions can be made for curves D and E because the history of the powder previous to the excitation for curve E is not known. Curve D followed B immediately, but some preliminary work without killing off was done before killing off for curve E.

The changes produced in the decay curve by varying the temperature at which excitation and decay take place are shown in

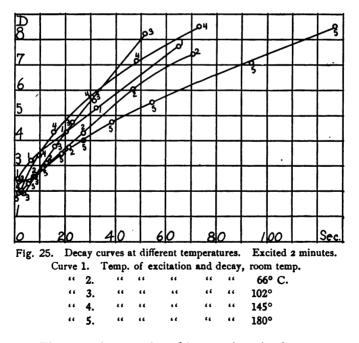
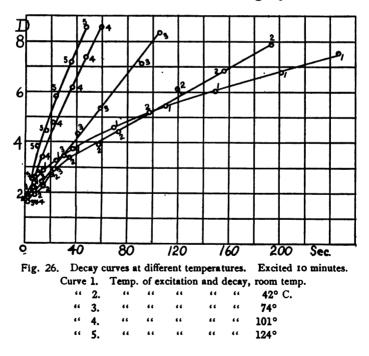


Fig. 25. The part that previous history plays in these curves cannot be estimated accurately, but its effect is small because the exci-

tation, which is relatively a long one, was not changed during a set of curves. The curves were taken in the order that they are numbered. Curve 1, taken at room temperature, is similar to the typical decay curves shown in Fig. 24. As the temperature is raised the curves pass through a series of changes. Curve 2 begins concave upward but changes during the decay to concave downward. Curve 3 is practically a straight line throughout. As the temperature is raised still further, the curves again become concave downward throughout, differing not widely from the typical decay curves at room temperature.

Another set of curves similar to those in Fig. 25 is shown in Fig.



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The effect of previous history is shown in Figs. 27 and 28. These curves might readily be mistaken for curves showing the

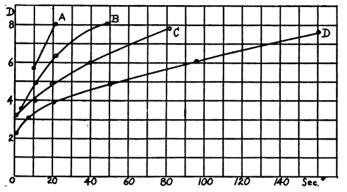


Fig. 27. Effect of history previous to excitation. Excitation and decay at room temperature. Excited 30 seconds. Curve A, excited after killing off with infra-red; curve B, excited immediately after curve A; curve C, excited immediately after curve B; curve D; before exciting for curve D, the powder was excited for 10 minutes and allowed to decay to an intensity corresponding to D = 9 in the figure, at which time the excitation of 30 seconds was begun.

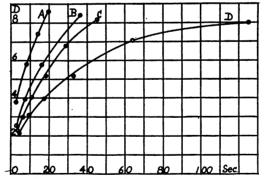


Fig. 28. Repeated curves in Fig. 27 at a temperature of 133° C.

effect of varying the length of excitation. Fig. 29 also shows the effect of previous history combined, however, with the effect of temperature.

The decay of phosphorescence in the case of Balmain's paint was

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These curves were plotted with intensity (I) and time as coordinates. For the sake of comparison, several of these curves have

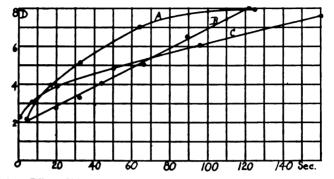


Fig. 29. Effect of history previous to excitation. Excited 30 seconds. Before each excitation, the powder was excited for 10 minutes and allowed to decay to an intensity corresponding to D = 9, at which time the excitation of 30 seconds was begun.

Curve	С,	Excitation	and	decay	at	room temp.
**	В,	**	**	"	"	88° C.
**	A,	**	"	**	"	133°

been replotted in Figs. 30 and 31 with  $1/\sqrt{I}$  and time as coordinates. Fig. 30 shows the effect of varying the length of excitation.

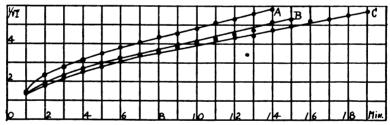


Fig. 30. Effect of varying the length of excitation. Excitation and decay at a temperature of 18°C. (Replotted from the data of Micheli.)

Curve	A,	excited	5 :	sec.
" "	В,	**	20	" "
	С,	**	300	"

Another curve excited for 60 sec. coincided almost exactly with curve C.

Fig. 31 shows the effect of varying the temperature at which excitation and decay take place. These curves and the curves given earlier in this article agree generally. Fig. 31 shows the effect of excitation and decay at a temperature lower than any used in this article.



In the case of calcium sulphide, it is not necessary to use a spectrophotometer to prove that there is more than one band included in the phenomenon of phosphorescence, for under the influence of

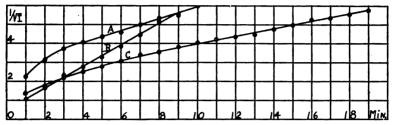


Fig. 31. Effect of varying the temperature at which excitation and decay takes place. Excited 300 seconds. (Replotted from the data of Micheli.)

Curve	A,	temp.	of	excitation	and	d	ecay,	— 21° C.
**	В,	"	"	**	* *	t.	"	100°
**	С,	"	"	66	"			18°

heat, the powder can be seen to change color, changing from a blue to a green. It has already been shown that the form of the phosphorescence decay curve may be closely approximated on the basis of two bands, each following the law,

$$I = \frac{\mathrm{I}}{(a+bt)^2}.$$

This explanation was carried to some length in the author's article on Sidot blende. But there seems to be no way of combining two decays each of which follows this law so as to produce an upward bending. If it be supposed that one band increases in intensity as the other decreases, then an upward bending is possible; but a downward bending is impossible unless both the bands subsequently decay together. This suggests that one of the bands is due to some secondary effect, instead of being produced by the exciting light. Such a band would increase in intensity a certain length of time, then decrease in intensity. If we suppose that the first band follows the law suggested, and that the second band follows the same law after it has reached its maximum intensity, then the discussion given in the article on Sidot blende still holds good, the supposition being that the second band is completely formed before the first point on a curve can be measured. If, however, conditions can be changed so

that a point can be observed before the second band is completely formed, then the curve will show initially an upward bending, as in curve 2, Figs. 25 and 26. If a band is formed by some secondary effect it will usually be present in the fluorescence spectrum because the excitation is continued long enough for the band to be formed.

The effect of previous history can be explained without adding any complications to the ideas already set forth. In the case of Sidot blende, it was undoubtedly the band of longer wave-length that decayed the slower. The same is true, probably, for calcium sulphide, for the color changes from blue to green when the powder is heated. In the case of the decay curve at room temperature, the intensity is too small for the change in color to be recognized by the eye. Assuming that the band of longer wave-length decays more slowly, and that this band is due to some secondary effect, then the action of repeated excitations without intervening killing off by infra-red might be to increase the intensity and to decrease the rapidity of decay of the second band without introducing any change in the rapidity of decay of the first band. Some indications of these effects can be seen in Figs. 27 and 28.

It is unfortunate that the curves in Figs. 27 and 28 were not taken in the reverse order, *i. e.*, excitation of long duration followed by shorter excitations. Such curves, according to the ideas just set forth, should show parallelism after the decay had proceeded some time. In an article on Sidot blende by Nichols and Merritt,<sup>1</sup> several sets of curves were taken in this order and they exhibit parallelism after decaying a short time.

To make any attempt to explain completely the curves in Figs. 25 and 26 on the basis of a second band due to secondary causes is impracticable because the problem is complicated by the addition of the effect of temperature. One assumption will necessarily have to

#### **No. 6.**] STUDIES IN THERMO-LUMINESCENCE.

was exposed to infra-red rays, then excited and allowed to decay at room temperature, heating being begun at a definite point on the decay curve. The coordinates for these curves are intensity (I) and time. Figs. 32 and 33 show the effect of varying the length of excitation. The double flash mentioned in the case of Sidot blende is plainly evident in the curves, and in the experiment was evident to the unaided eye. The color also varied, being blue for the first flash and a yellowish green for the second. At the longest excitation, the second flash is barely visible in the photometer, the only

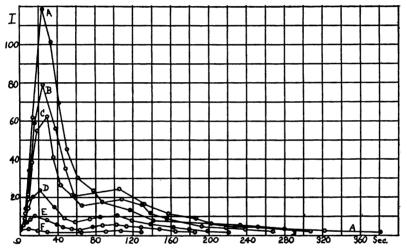


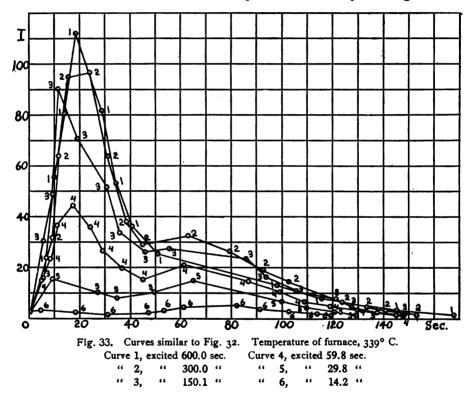
Fig. 32. Effect of varying the length of excitation. Excited and allowed to decay at room temperature to I = 2.9, when heating was begun. Temperature of furnace, 277° C.

Curv	e A, e	xcited	600.2 sec	. Curve	: D, e	xcited	60.7 sec	:.
"	В,	"	300.0 "	" "	Ε,	""	30.1 "	
66	С,	" "	150.1 "	64	F,	**	14.8 "	

evidence of its existence being a slowing up in the rate of decay. As the length of excitation is decreased, the second flash becomes, relative to the first, greater and greater.

At lower temperatures the second flash becomes less evident, and the peculiarity of the curve for 600 seconds excitation, as shown in Figs. 32 and 33, no longer exists. For the lower temperatures the second flash for 600 seconds excitation is greater than that for any shorter excitation at the same temperature. At a temperature near 100° C., the second flash is no longer evident in the curves.

It is evident that two bands are represented in the preceding curves. Any one of these curves is probably made up by the superposition of two curves, each of these component curves representing the



flash for one of the bands. If one considers the first flash in Figs. 32 and 33, it will be seen that the curves resemble closely corresponding curves shown in the article on Sidot blende. The maximum intensity increases with length of excitation and occurs later and later. The areas included between the curves and the coördinate axes increase with the excitation. The effect of saturation is shown both by the change in areas and by the change in the maximum.

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if one considers the first flash alone, the curves are similar to those already published for Sidot blende. Fig. 35 shows the maximum intensities of the first flash plotted against temperature.

The second flash does not always follow the laws of the first flash

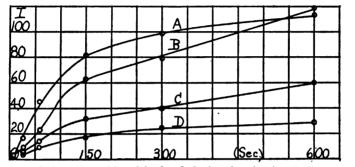


Fig. 34. Maximum intensities of the first flash plotted against length of excitation.

Curve	1,	temp.	of	furnace	339° C.	(From	Fig.	33)
"	2,	"		"	277°	("	"	32)
"	3,	"	"	**	222°			-
**	4.	**	"	"	148°			

as can be seen in Fig. 33. As the length of excitation is increased, the maximum intensity of the first flash occurs later and later, while the maximum of the second flash occurs earlier and earlier. This effect is not well defined in Fig. 32, due perhaps to the fact that the

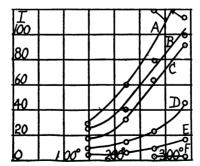


Fig. 35. Maximum intensities of the first flash plotted against temperature of the

flash is of smaller intensity and consequently more difficult to follow accurately. Fig. 36 shows the effect of saturation for the second

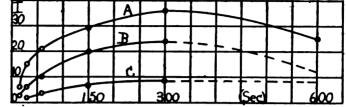


Fig. 36. Maximum intensity of the second flash plotted against length of excitation.

Curve A, temp. of furnace, 339° C. (From Fig. 33) " B, " " " " 277° (" 32) " C, " " " 222°

flash. These curves indicate that an increase in the length of excitation beyond a certain length does not increase the maximum intensity but decreases it. There is a slight possibility that the change in maximum intensity noticed for an excitation of 600 sec-



Fig. 37. Maximum intensity of the second flash plotted against temperature of the furnace. Curve B. excited 300 sec.

Curve	: <i>B</i> ,	excited	300	sec.
**	С,	66	150	"
""	D,	**	60	**
**	E,	**	30	**
"	<i>F</i> ,	" "	15	"

onds may be due to previous history, the excitation of 600 seconds always being the first run of a series. In contradiction to this is the fact that a practice run almost always preceded the series. Furthermore, the peculiar change in the second flash does not exist for lower temperatures, as curve C, Fig. 36, and other curves, indicate.

The relation between the maximum intensity of the second flash and the temperature is shown in Fig. 37. This figure corresponds



closely to Fig. 35, which shows the corresponding relation for the first flash.

Fig. 38 shows the effect of delay in heating. Fig. 39 shows the same curves plotted with time measured from the beginning of

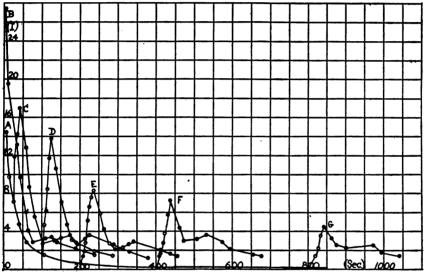


Fig. 38. Effect of delay in heating. Time measured from the end of excitation. Excited 60 seconds at room temperature. Temperature of furnace,  $228^{\circ}$  C. Curve A, decay at room temperature. The time between the end of excitation and the beginning of heating is as follows:

Curve	<i>B</i> , 2.1 s	iec.	Curve	Ε,	203.2 se	c.
"	C, 25.6	**	"	F,	401.7 "	"
**	D, 101.7	" "	"	G,	801.7 '	"

heating. Here again, if one considers the first flash alone, the curves are similar to those shown in the case of Sidot blende. The longer the delay in heating, the less intense the flash, and the later the maximum intensity of each flash. Furthermore, the time of decay for curves at one temperature and constant length of excitation is constant. It is difficult to make any deduction from the points representing the second flash.

Another set of curves similar to those shown in Fig. 38 is shown

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It is difficult to say how much difference exists between the behavior of Sidot blende and Balmain's paint. The decay curves

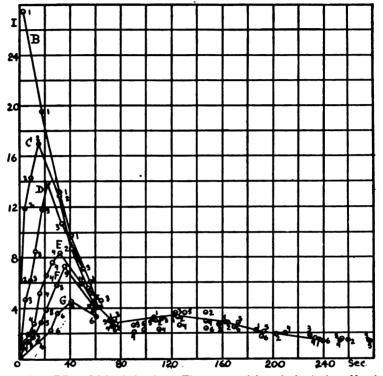


Fig. 39. Effect of delay in heating. Time measured from the beginning of heating. Same curves shown in Fig. 38.

at room temperature are very much alike. As the temperature is raised both decay curves become straight lines, but Balmain's paint shows a transition through a double curvature decay before reaching the straight line decay, while Sidot blende does not exhibit this phenomenon. Above the temperature at which the decay curve becomes straight, Balmain's paint shows a decay approximating the decay at room temperature, while in the case of Sidot blende the decay is too rapid to be followed with the available apparatus. The decay of Sidot blende is so rapid that one cannot get enough points on a curve to say positively that it does not exhibit double curvature at temperatures much higher than room. In the cases where the powder is heated after excitation, Balmain's paint shows - <sup>-</sup> .

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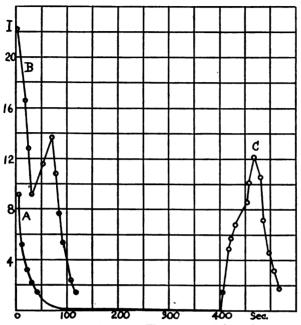
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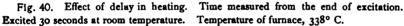
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a double flash under some conditions, and one flash under other conditions, while Sidot blende shows one flash under all conditions,





Curve A, decay at room temp. "B, waited 2 sec. after excitation before heating. "C, "400 " " " " "

unless it be admitted that there are indications of a double flash in some of the Sidot blende curves, in which case the two substances show substantially the same curves. Considering the first flash only, there is perfect agreement between the curves of Sidot blende and Balmain's paint. The action of infra-red is more marked in the case of Sidot blende, but otherwise, there is no marked difference. The fluorescence spectrum shows two bands in the case of each substance, but there is one point of difference, in that the band of shorter wave-length is more prominent in the case of Balmain's paint and less prominent in the case of Sidot blende than the band of longer wave-length.

PHYSICAL LABORATORY, CORNELL UNIVERSITY. (Contribution from the Cryogenic Laboratory of Wesleyan University.)

# EFFECT OF MECHANICAL VIBRATION UPON CARBON DIOXIDE NEAR THE CRITICAL TEMPERATURE. II.

#### BY W. P. BRADLEY, A. W. BROWNE AND C. F. HALE.

I has already been shown<sup>1</sup> that saturated carbon dioxide within a couple of degrees of the critical temperature is extraordinarily sensitive to minute but sudden increase of volume and thus gives rise under suitable conditions to fog effects. The fog consists of droplets temporarily suspended in the vapor phase or of gas bubbles similarly suspended in the liquid phase.

It was also shown that when the well-known Cailletet liquefaction apparatus is used such fog may be produced by mechanical vibration communicated to the mercury column from without. This may be accomplished most effectively by means of a steel rod clamped horizontally to the body of the apparatus and made to vibrate vertically. Certain quantitative relations between the frequency of vibration and the condition of the carbon dioxide were also given and discussed in the former paper.

In the present paper it is proposed to set forth certain observations which though qualitative in their nature appear to merit attention.

#### DYNAMIC AND RESIDUAL FOG.

If the carbon dioxide system is in a state of thermal equilibrium, sufficiently gentle vibrations produce *dynamic* fog — that is, fog which clears up at once when the vibrations are interrupted. On

Residual fog appears denser in transmitted light than the dynamic fog which immediately precedes it, while by reflected light the reverse is true. The theory already advanced,<sup>1</sup> according to which the dynamic fog is produced by intermittent expansion of the system, affords ready explanation of the first of these facts. Dynamic fog is discontinuous; it exists only in pulses. Between the pulses light has unobstructed passage.

An explanation of the action of reflected light is not so immediately apparent. Residual fog, being continuous, might be expected to reflect more light than dynamic fog, which is intermittent. However, dynamic fog doubtless consists of droplets or bubbles which are both more numerous and in part at least larger than those of residual fog. Those which are produced earlier in the fall of the mercury column would naturally, as expansion progresses, become larger than such as begin to form later. Conversely, at the return of the column they would persist longer. Residual fog could only consist therefore of such droplets or bubbles as had once been large and were now very much reduced in size. It will be understood of course that all of these, both large and small, are of microscopic size and that the terms "large" and "small" are used in a relative sense only.

An explanation is yet lacking of the fact that residual fog can exist at all under thermal equilibrium. According to the theory fog forms only during one quarter of the complete vibration — that is, during the time when the mercury column passes from its initial position of rest, which is also the equilibrium point, to the lowest limit of its oscillation. Fog is disappearing on the other hand during the next quarter of the vibration while the column approaches the equilibrium point again. As these periods are equal in length and opposite in direction the expansion of the first should be exactly offset by the compression of the second, and the condition of the carbon dioxide at the end of the second quarter should be in so far exactly the same as at the beginning. In other words

#### THE SENSITIVENESS OF THE SYSTEM.

The sensitiveness of the carbon dioxide to vibrations depends on two classes of factors. The first class includes such as relate to the form and construction of the Cailletet apparatus, and which may therefore be termed *external*. The second class includes such as relate to the condition of the carbon dioxide, and may therefore be called *internal*. Among the external factors affecting sensitiveness are, (a) the relative volume of the pressure jacket, (b) the thickness of its walls, and (c) the internal diameter of the pressure tube.

(a) It is obvious that if the pressure tube opens into a pressure jacket the volume of which is very large in comparison with that of the carbon dioxide, a very minute yielding of the walls of the jacket will suffice to produce a relatively large change in the volume of the carbon dioxide. In these experiments the ratio between the volume of the jacket and that of the compressed carbon dioxide varied from 1260: I when the carbon dioxide was nearly all vapor, to 1760: I when it was nearly all liquid.

(b) The thickness of the walls of the pressure jacket will largely determine to what extent those walls will yield under given circumstances. Their thickness doubtless will also determine in the main the general range of the pitch of the vibrations to which they shall easily respond. Thick walls might be expected to respond most satisfactorily to vibrations of higher frequency, and *vice versa*. To investigate such factors as the two just mentioned would require experiments with a number of pressure jackets of varying construction.

(c) The width of the tube in which the carbon dioxide is contained proves to be of prime importance. Experiment shows that the wider the tube the denser is the fog, other conditions being the same. This was to have been expected, since in a wide tube vibrations of given amplitude produce a greater change in the volume of a given mass of substance than is the case in a narrow one. Moreover as the change of volume produced by such vibrations varies with the

becomes quite incapable of adiabatic expansion. Indeed very narrow tubes such as are frequently used in the prosecution of critical temperature work are quite unsuited to the kind of observations here described. An internal diameter of 5 mm. is desirable, and tubes of much larger diameter may be used to great advantage.<sup>1</sup>

The internal factors affecting the sensitiveness of carbon dioxide include (a) temperature, (b) location of the meniscus, (c) vertical distance from the meniscus.

(a) Of these, temperature is by far the most important. When the carbon dioxide is in thermal equilibrium residual fog practically cannot be produced, in such an apparatus as we have used, at a temperature below 30° C. Above 30° the difficulty decreases at a remarkably accelerated rate. In fact at about 31.1° or 31.2°, the meniscus being still visible, it is difficult to avoid residual fog. Moreover the latter becomes singularly dense and white, reminding one in a way of hard drifted snow<sup>3</sup>. The duration of residual fog, once produced, goes hand in hand with the sensitiveness of the carbon dioxide to its production. At 30° it would hardly be noticed at all by one who was not looking for it, so quickly does it disappear. At 31.1° or 31.2° on the other hand it has been observed to last for 16 seconds in a phase of only 5 mm. depth. Doubtless there are at least three reasons for this. In the first place at the latter temperatures a greater amount of fog is produced, so that more time is required for the evaporation of the droplets or for the absorption of the bubbles. In the second place the texture of the fog is coarser, which also delays evaporation and condensation respectively. Thirdly, settling is much slower in close proximity to the critical temperature, for the evident reason that the densities of the two phases become so nearly alike in that region.

<sup>1</sup> It may be remarked in this connection that tubes of considerable internal diameter, if properly prepared and mounted, are capable of withstanding critical pressures without possessing unusual thickness of wall. Thus with the 5 mm. internal diameter and 1 mm. thickness of wall an average tube of Jena glass will withstand a pressure of 200 atmospheres before bursting. The same may be said of ordinary soft German glass though the latter is considerably more erratic in its conduct. Bradley & Browne, At 31.1° to 31.2° is found the maximum sensitiveness of the carbon dioxide to the production of dynamic fog also — a sensitiveness which always greatly surpasses the other, as has been stated.

The reason is probably to be sought in part in the situation as to latent heat at that temperature. The real barrier to sudden passage from the liquid to the gaseous state or the reverse is latent heat. The smaller the latent heat the greater is the mass of substance which can be changed from one physical state to the other by the expenditure of a given amount of energy. Now the latent heat of any substance decreases very rapidly as the latter approaches the critical temperature and the barrier between the liquid and the gaseous state is correspondingly lowered. Less and less energy is thus required to transform a visible mass of substance from one state to the other.

If this were the only consideration however, the maximum of sensitiveness should be reached exactly at the critical temperature, which is not the case. From 31.2° upward the sensitiveness decreases again very rapidly, owing perhaps to the rapidly approaching equality of density and therefore of optical properties as between the droplets or bubbles on the one hand and the medium in which they are suspended, on the other.

(b) Even with perfect thermal equilibrium, dynamic fog is seldom of equal density in the two phases of the carbon dioxide. It may even be lacking altogether in one of them. Its location in one or the other of the phases, or the relative densities, if it is present in both phases, are found to depend partly upon the relative volumes of the phases — that is, upon the height of the meniscus — and partly on the amplitude of the vibrations.

In general when the vapor phase is subordinate in volume, or in other words when the meniscus stands high, the gentlest bowing which is effective at all produces for in the vapor phase only. With

The reason for this disparity in sensitiveness is not far to seek. As the specific compressibility of the vapor phase exceeds that of the liquid a greater share of the expansion to which the system as a whole may be subjected falls to the lot of the vapor phase. This general superiority of the vapor phase in point of sensitiveness is of course greatly accentuated when its volume is least — that is, when the carbon dioxide is all but wholly in liquid form, for then a given amount of expansion bears a larger ratio to the total vapor volume.

On the other hand if the meniscus stands sufficiently low and the liquid volume is made sufficiently subordinate the whole situation is reversed. Fog appears first in the liquid phase and afterwards, with greater amplitude of vibration, in the vapor. However, a much stronger vibration is required in this case to produce any fog at all.

It would naturally follow from the foregoing that at a temperature very near the critical, where the two phases become practically identical,<sup>1</sup> equality of fog density should be secured when the latter are present in equal volumes. That this is only approximately true may perhaps be accounted for by the unequal influence of gravity on the two phases. The force of gravity tends to assist the formation of droplets in the vapor phase and to hinder their evaporation when formed, while it restricts the formation of bubbles in the liquid phase and assists in their recondensation. Moreover its effect on the bubbles is greater than on the droplets, because the former are subject to the weight of both liquid and vapor.

For temperatures further from the critical, but still within the egion now under discussion, a correspondingly lower position must be chosen for the meniscus, if equality in fog density is to be secured. This may be accounted for by the greater difference between the densities of the liquid and vapor phases at lower temperatures.

<sup>1</sup> In the use of the term "identical," it should be understood that nothing is implied as to the homogeneity of either phase near the critical temperature. Whatever difference of view may prevail as to the nature of the critical state it can doubtless be shown that if the two phases are kept in equilibrium, either mechanically by mixing, or by diffusion through sufficiently long contact with one another, they do become identical at the critical In the phase of greater density greater inertia must be overcome locally during such rapid fluctuations of volume as are involved.

The foregoing discussion is based on observations taken at stationary temperatures<sup>1</sup> and during equilibrium between the two phases. That the first of these two conditions does not of necessity imply the second cannot be too strongly insisted upon.

Near the critical temperature, as is well known, small differences of temperature correspond to great differences of condition in the two phases, and the phases themselves meanwhile are so nearly alike that these differences of condition require a very considerable time for readjustment, unless the process is hastened artificially. Among the devices often employed for such a purpose may be mentioned the use of a bit of iron caused to move about within the system by means of a magnet held outside, and the practice of frequently reversing the (Natterer) tube so as to bring the phases into intimate mechanical contact with one another. These methods were impracticable in our experiments and they were also unnecessary, for it was found that strong bowing of the vibratory rod was an effective substitute. In this way, an agitation of the carbon dioxide could be induced which was veritably tempestuous, particularly so if the bow was held at a certain angle from the vertical. Equilibrium between the phases was recognized as established when gentle bowing produced a constant result after several such periods of turmoil.

#### EFFECT OF RISING OR FALLING TEMPERATURE.

Starting at thermal equilibrium, raising the temperature of the carbon dioxide by a small amount has the effect of shifting the fog downward, either wholly or in part, out of the vapor into the liquid. Moreover the fog becomes residual and is produced by the slightest touch of the bow. That this should be so is not strange. Rise of

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The sensitiveness of the fog as a test for detecting minute changes of temperature is extraordinary. The thermostat<sup>1</sup> which we employed during the period of our most careful observations was capable of maintaining constancy of temperature to one thousandth of a degree Centigrade for a considerable period of time, and the Beckmann thermometer with its electrical vibrator enabled us to read temperatures to one or two thousandths of a degree. So sensitive however are these fog effects as an indication of thermal change, that variations in temperature of even this order were heralded by the fog many seconds before they became apparent otherwise.

In the study of unsaturation and supersaturation, two methods were employed for securing minute thermal changes in the carbon dioxide.

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One of these consists in slightly decreasing or increasing the volume of the carbon dioxide, and so in temporarily raising or lowering its temperature by adiabatic compression or expansion. This can easily be done by slightly opening for a moment the needle valve, which closes communication between the steel pressure jacket of the Cailletet apparatus and the hydraulic pump which develops the pressure. If the pressure in the pump is made slightly greater or less than that which prevails in the Cailletet apparatus, a slight opening of the valve for a moment permits a minute amount of water to enter or to leave the pressure jacket, so as respectively to decrease or increase the volume of the carbon dioxide. In this way it was possible to change the internal temperature of the carbon dioxide suddenly in either direction, and then to watch the phenomena attending its gradual recovery. In connection with such a study some rather curious effects were observed.

If the bath temperature is very near the critical, and the height of the meniscus is such as to correspond to dynamic fog in the liquid, a very minute decrease in the volume of the carbon dioxide causes the meniscus suddenly to disappear, in consequence of the rise of temperature produced by the compression. Suitable bowing now produces very dense dynamic and residual fog in the whole region just occupied by the vapor, and none at all in that which contained the liquid. The lower limit of the fog is the disc where the

<sup>1</sup> Bradley and Browne, Journal of Physical Chemistry, 6, 1902, 118-135.

meniscus formerly was, and the limit is just as sharply defined as if the meniscus were still there. Presently as the heat of compression becomes gradually dissipated, the meniscus suddenly reappears, but on a higher level, within the fog zone. Still the latter continues for a time to be bounded exactly as before, until the thermal equilibrium between the carbon dioxide and the bath is almost complete. Then, according to circumstances, there may be noticed one of two things. If the meniscus is still low enough to correspond normally to fog in the liquid only, fog presently appears in the older liquid region also and becomes rapidly denser, while that above the old position of the meniscus grows thinner. Finally, with sufficiently gentle bowing, the fog disappears entirely in the vapor phase above the new meniscus, and extends throughout the whole of the liquid from the new meniscus down to the mercury. In the other case, when the new meniscus is high enough, the fog in the region between the new and the old meniscus gradually thins until finally the fog is confined to the zone above the new meniscus. Which of these alternatives carries the day depends, as has been said, upon the height of the new meniscus --- whether it normally corresponds to fog in the liquid only, if still low enough, or to fog in the vapor only, if at a higher level.

The noteworthy feature of the situation is that newly formed liquid is not allied in sensitiveness to the older liquid at all, but to what remains of the vapor phase. Clearly the new liquid is saturated like the vapor, while the old liquid for a time is not. The sharpness of the fog line between the new and old liquid appears to be due to differences of density of considerable magnitude, and not in general to any inability of the two to mix with one another, for the turmoil produced by firm bowing does mix them and throws the fog limit at once up to the new meniscus.

For the most part there was nothing whatever except the fog phenomena to indicate the boundary between the two layers of liquid. Twice an additional phenomenon occurred, namely, the existence of two visible menisci in the system at once — the new permanent one above, and a temporary one, which appeared where the old one had been, lingered a moment and then disappeared, leaving only the fog limit to mark the spot as before. Every effort

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which ingenuity could suggest was employed to multiply instances of this sort, but without result. It would have been natural to conclude that both of the cases mentioned were an illusion, if it were not that each was observed by two operators simultaneously.

A sequence of phenomena which is in part the reverse of that already mentioned as attendant upon slight but sudden compression of the carbon dioxide may be established by correspondingly increasing the volume by a slight amount. In this case the meniscus naturally does not disappear, but drops suddenly to a lower level. The expansion results in the immediate appearance of dense fog in both phases. If left undisturbed, the fog becomes thinner and finally disappears, while the meniscus gradually descends to a still lower level. During this process gentle bowing thickens the fog from the bottom of the liquid up to the point from which the meniscus is gradually receding - an indication that the vapor newly formed from the liquid is both denser and more saturated than that of longer existence. The upper limit of the fog is very sharply defined. Continuation of the gentle bowing results finally in dynamic fog on only one side of the meniscus, according to the height of the latter, as previously explained. At any time in the process, firm bowing causes at once all difference in sensitiveness between the older and the newly formed vapor to disappear.

The other method of changing the temperature of the carbon dioxide is the obvious one of gradually changing the temperature of the bath. Naturally it is much more time-consuming, but on the other hand the results are simpler. In this case, the vapor phase is always unsaturated during rising temperature, and yields fog with difficulty or not at all, while the liquid is supersaturated and yields both dynamic and residual fog. When the temperature is falling the reverse is true.

As the position of the meniscus changes very gradually indeed by this method of altering the temperature, there is practically no opportunity for the study of differences of sensitiveness between new and old liquid, and between new and old vapor respectively, unless all bowing of the vibratory rod is discontinued for a considerable period of time, during which new liquid or new vapor accumulates somewhat in the absence of agitation.

The influence of strong bowing as a means of changing existing relations between the two phases has been mentioned already. further instance may be given at this point before leaving the subject With the carbon dioxide at a temperature which is of fog zones. constant and very near the critical, and with the meniscus at about the height proper for equality of density in the dynamic fog of the two phases, sufficiently firm bowing produces a condition resembling opalescence in the whole system, attended, as before explained, by wild confusion in the region of the meniscus. If the bowing is then interrupted, the meniscus settles at once into place and the opalescence gives way to a belt of residual fog of great density, which finally disappears, partly by settling and partly by absorp-This belt extends to approximately equal distances on each tion. side of the meniscus. The width of the belt depends on the duration of the bowing. If the firm bowing is then renewed without waiting too long, the belt gives way at once to the former opalescence of dynamic fog. Once, because of some peculiar handling of the bow no doubt, this second opalescence was succeeded by a system of six sharply defined zones, four of which consisted of residual fog. At the center was a dense belt as before, cut in two by the meniscus. On the upper and lower sides of this belt was a layer of thinner fog, and beyond this in either direction a zone of no fog at all. On every other occasion a second bowing resulted like the first in a single belt of residual fog, or in other words, a system of four zones with the meniscus in the center. The belt however was wider than before. Whatever the number of zones may be, the boundaries are in all cases absolutely sharp and horizontal, and within any given zone no shading off in density is to be observed in either direction.

(c) Sensitiveness at the Meniscus.— In a system which is in a condition of equilibrium as nearly perfect as constancy of temperature in the bath, occasional firm bowing, and time can make it, the very gentlest bowing which is capable of giving a visible result produces dy-

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In the theoretical case of perfect equilibrium between the two phases we can think of no cause for such a phenomenon except gravity, whose influence would be equivalent to that of slightly greater pressure in the lower part of each phase than in the upper, and would result in so far in a maximum tendency to condensation at the bottom of the vapor, and in a maximum tendency to the formation of vapor at the top of the liquid. In any attainable approximation to perfect equilibrium, the meniscus, where the two phases are in contact with each other, is of course the region of greatest saturation, and ought therefore to be most sensitive.

In any case, one useful effect of this thickening of dynamic fog toward the meniscus is to define the position of the latter with great Particularly is this true when the fog lies on both sides precision. Such an aid to observation gains increasingly in value as the of it. critical temperature is approached and the meniscus itself becomes thinner, flatter and all but invisible. In fact --- and this was a great surprise - even in our most careful experiments it was possible to define the boundary between phases (?) at a temperature .15 of a degree above the point at which the meniscus became entirely invis-No attempt was made to determine for how long a time this ible. fog line would continue above the critical temperature. But it was noted several times after a lapse of 15 to 20 minutes, and once after about half an hour. Within these time limits at any rate it never failed to appear as a result of proper bowing. Its density however was very slight. In fact the point of maximum density in dynamic fog appears to lie about one tenth of a degree below the critical temperature, as has been said, and the sensitiveness decreases very rapidly from this point upward.

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#### CRITICAL TEMPERATURE OF CARBON DIOXIDE.

As the carbon dioxide which was employed in these experiments was of rather unusual purity, containing only from two ten-thousandths to twenty-five millionths of gas unabsorbed by potassium hydroxide,<sup>1</sup> it may be of interest to record observations which were made of its critical temperature.

Of course the ideal position for the thermometer in such determi-

<sup>1</sup> The preparation of this gas will be described in a subsequent paper.

nations is inside of the pressure tube itself, wholly immersed in the substance under examination. But this was impossible under the circumstances, and the method employed was the usual one of raising and lowering the temperature of the bath very slowly indeed, and noting the point at which the meniscus disappeared and reappeared. The lag of the carbon dioxide was corrected in part by occasional firm bowing. The average differences of temperature between the disappearance and the reappearance of the meniscus was .08 of a degree, and the mean value of the critical temperature itself was 31.26° (cor.). The thermometer was standardized by the use of fused sodium sulphate crystals, the transition point of which was taken as 32.383°.<sup>1</sup>

WESLEYAN UNIVERSITY, MIDDLETOWN, CONN., February 6, 1908.

<sup>1</sup>Zeitschrift für physikalische Chemie, 43, 1903, 471.



# RADIOACTIVITY OF A SMOKE LADEN ATMOSPHERE.

#### BY S. J. ALLEN.

IN this paper are expressed a number of results obtained on the radioactivity of the air at Cincinnati during the past year. Since the radioactivity of the atmosphere is such a wide-spread phenomenon, and differs both in amount and rate of decay in different localities, it is of interest that as many observations as possible be made under varying climatic conditions.

Some years ago at Montreal, the author made a series of observations <sup>1</sup> on the rate of decay and found it to be approximately exponential, falling to half value in about 45 minutes. On several occasions, however, the period varied from 38 to 60 minutes and some indications were obtained of an even slower rate of decay. It was then suggested that the general rate of decay was not simple but the resultant of several rates of decay each differing from the others.

Since that time observations have been made by various investigators in different parts of the world, all leading to the same result that the rate of decay in general is not simple. Bumstead and Wheeler<sup>2</sup> at New Haven showed that the air drawn from the soil a that place contained radium emanation, and by exposing a negatively charged wire, obtained on it an excited activity identical with that due to radium. It was also shown that a small amount of thoriumexcited activity was present. Blanc<sup>3</sup> working at Rome found that the activity on a negatively charged wire after a long exposure, showed clearly the presence of thorium-excited activity.

Eve <sup>4</sup> at Montreal has made a number of investigations on the radioactivity of the atmosphere and has obtained evidence to show that the amount of radium emanation present in the free atmosphere

<sup>1</sup>S. J. Allen, Phil. Mag., 1904.
 <sup>3</sup> Bumstead & Wheeler, Am. Jour. of Science, 1904.
 <sup>3</sup> Blanc, Phil. Mag., 1906.
 <sup>4</sup> Eve, Phil. Mag., 1907.

is of the right order of magnitude to account for the greater part of the effects observed. Quite recently he has shown by a direct experiment the presence of the emanation in the free air.

The air at Montreal in the winter time is generally very dry, cold, and free from smoke particles, whereas the conditions at Cincinnati are quite the reverse, the amount of finely divided smoke particles in the air being very large. The object of the present investigations was to obtain a large number of decay curves under different atmospheric conditions, and by comparing one with the other, and analyzing them, to obtain if possible the simple rates of decay common to one or more.

If the radioactivity of the atmosphere is due to the presence of radium, thorium, and possibly actinium distributed throughout the crust of the earth, we would naturally expect the rate of decay to be in general very irregular and to be made up of the separate rates of decay of the excited activities of the above radioactive elements. Since the rate of decay of the radium emanation is slow, falling to half value in about 3.86 days, there would be time for it to diffuse uniformly throughout the atmosphere and to a considerable height above the earth, and yet retain a sufficient amount of activity to cause the results observed. On the other hand the emanations of thorium and actinium decay too rapidly for them ever to reach very far, if at all, above the earth. That part of the radioactivity of the air which is due to radium and thorium must be occasioned by their excited activities, and not their emanations.

We would thus expect the activities due to radium to be always present and to constitute the larger amount, while the effects due to the thorium and possibly actinium would be very irregular both in occurrence and amount.

It is then possible to have present in the free atmosphere radium emanation, radium A, radium B and radium C; thorium A and

the two wires passing through two holes in a sheet of ebonite placed under a window. The other pulley was fastened to a building about 180 feet away, the insulation of this pulley being protected from the rain, snow and moisture by a metal hood. By rotating the inner wheel the activity could be removed quickly from the wire without going outside the building. The distance of the wire above the ground was about twenty feet.

The wire was used under three conditions :

1. It was charged negatively by an influence machine up to potentials of 5,000 to 40,000 volts.

2. It was charged positively.

3. It was not charged at all.

The radioactive substance obtained on the wire was removed in several different ways.

(a) A piece of leather moistened with ammonia was rubbed over the wire.

(b) A piece of wood with a groove cut to fit over the wire, and moistened with ammonia, was used.

(c) A piece of lead wire, suspended underneath the copper wire during exposure, was afterwards wound on a form into a flat spiral and tested.

(d) A piece of fine linen was rubbed lightly over the wire without any ammonia.

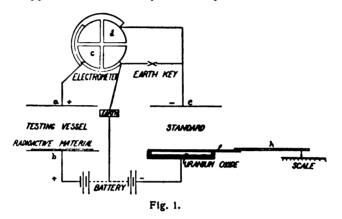
The rate of activity decay was obtained in the usual manner by placing radioactive substance between two condenser plates and observing the saturation current as time went on. The first observation was taken from two to five minutes after removal of the charge from the wire. The ionization current was measured by a Dolezalek electrometer. In the early experiments the "rate of leak" method was used, but in the later ones the null method as incorporated by the author in his new null reading instrument.

This instrument is fully described in a recent article<sup>1</sup> and it will not be necessary to go into details here. A consideration of Fig. 1, will, I think, show clearly the working of the instrument. The quantity of electricity furnished to the charging quadrants by the radioactive substance is neutralized by an equal amount of opposite

<sup>1</sup>S. J. Allen, Phil. Mag., Dec., 1907.

sign obtained from an adjustable standard of uranium oxide. The standard is calibrated in proportional numbers, the maximum being taken as 100 per cent.

The balance point is independent of the capacity of the system and of the sensitiveness of the electrometer. The electrometer is thus only used as an indicating and not as a measuring instrument. With this apparatus the intensity of activity is obtained at the exact



instant of time considered, while in the "rate of leak" method, some little time is necessary to make a reading. Moreover the readings from day to day are always obtained in terms of a definite standard and are thus directly comparable with one another.

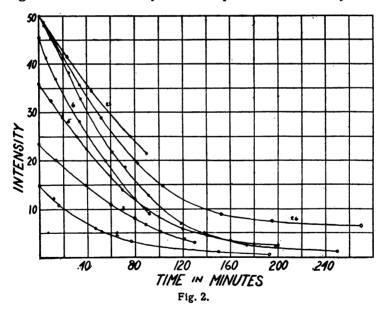
The error of observation in these curves is probably not greater than one per cent.

About fifty curves in all were obtained under varying conditions of the atmosphere, from a clear, dry, cold day, to a warm, moist and smoky one. On all occasions and under all conditions of collecting a measurable amount of raidioactivity was obtained. When the wire was charged negatively, the largest amount was observed, as one would expect. When the wire was charged positively only a small amount was obtained, while for an uncharged wire a very considerable quantity could be always collected. The maximum amount on the uncharged wire was as much as 30 per cent. of the maximum of that on the negatively charged one. Over a gram of soot could sometimes be collected on the wire, which was as active weight for weight as uranium oxide.



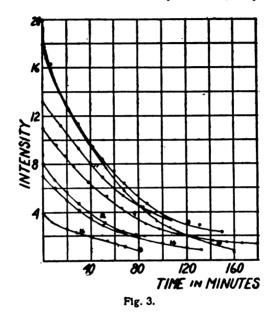
It was found that a piece of linen rubbed very lightly over the wire removed practically all the active substance in the case of the uncharged wire, but only 50 to 80 per cent. for the negatively charged wire. To get the remainder off the wire had to be rubbed over with a piece of cloth or leather moistened with ammonia. In the case of the charged wire the strong field draws some of the active carriers into close connection with the metal, while with the uncharged one the active substance is deposited lightly on the surface.

The interesting fact that the activity can be obtained on an uncharged wire is undoubtedly due to the presence of the finely divided



smoke particles in the air, as no such phenomenon was observed at Montreal, where the air is comparatively free from smoke. These particles act as collectors for the radioactive carriers. In falling through the air they carry with them the active matter, and are deposited on any surface they come in contact with. The results are eimilar to those observed by Miss Brooks<sup>1</sup> for the excite dactivity from a high altitude would probably only contain radium C, while the activity of the smoke particles being from a much lower altitude would be much more complex.

The period of decay of the activity from rain and snow as shown by the author and others is about thirty minutes, very close to that



of radium C, whereas as I shall presently show the period of decay for the activity near the earth varies from 36 to 80 minutes.

The results of the complete set of observations are expressed in the decay curves shown in Figs. 2-7. The ordinates represent the saturation currents in arbitrary units, and the abscissæ the times in minutes. Those curves which have the intensity plotted in per cent. are the ones made with the null instrument, while the others represent those by the "rate of leak" method.

In Table I. the data taken from these curves are expressed in a more convenient form for comparison. The intensities are all expressed in per cent. of the reading when the time is equal to zero. The numbers in the first column refer to the number of the curves in Figs. 1–8. Under "Remarks" are given some data as to the method of collecting and removing the active substance from the

## SMOKE LADEN ATMOSPHERE.

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# TABLE I.

### Intensity in Per Cent.

No.	80	60	50	40	30	25	20	12.5	6.3	3.1	Remarks.
1	21	42	54	68	83	93	103	125	164	230	Thin leather with ammonia
*2	12	24	36	48	60	70	80	112	166		Thick leather with ammonia
3	20	43	55	70	86	97	108	132			Thick leather with ammonia
4	18	38	49	62	79	89	102	122	160		Thick leather with ammonia
5	20	42	56	69	85	96	111	139	195	1	Thick leather with ammonia
6	15	35	46	61	75	83					Thick leather with ammonia
7	16	39	54	64							Thin leather with ammonia
8	13	30	42	56	67	80	94	122	163		Thick leather with ammonia
9	17	38	50	64	82	91	110	167			Lead wire — signs of slow rate of decay
10	17	35	44	56	70	78	90	118	150		Lead wire
11	17	37	48	60	77	82	94	122			Lead wire
*12	13	28	37	50	69	82					Lead wire
13	18	33	45	60	79	90	108	148		1200	Lead wire — signs of slow rate of decay
*14	14	29	39	52	68	79	100	124	-		Lead wire - signs of slow rate of decay
15	19	39	49	65	86	100	116				Lead wire — signs of slow rate of decay
*16	10	28	39	50	63	73					Wood with ammonia
17	19	40	52	66	90	109					Wood with ammonia, signs of slow decay
18	20	39	50	65	81	100					Wood with ammonia
*19	10	28	40	55	76	85	99				Wood with ammonia
20	22	44	57	70	86	94	104	131			Linen, wire charged negative, without ammonia
21	20	41	51	62	76	86	98	118			Linen, wire charged negative, without ammonia
22	<sup>•</sup> 25	55	72	88	107	119	132	163	220		Linen, wire charged 2 hours negative, without ammonia, slow
	i i										decay
23	28	59	77	98							Linen, wire charged negative, without ammonia, after 16 hours 10 per cent. left
24	16	37	48	60	78	86	95	116	150	194	Linen, wire charged 30 minutes negative, without ammonia
*25	11	29	40	52		86					Linen, wire charged 5 hours negative, without ammonia
26	22	47				117					Linen, wire charged 21 hours negative, without ammonia,
20		77		13	101		101	000			after 20 hours 4 per cent. left
27	16	30	42	60	80	94	110	120			Linen, wire uncharged, slow rate of decay
*28	15	31	39		71			132			Linen, wire uncharged
29	12	31	1	58			1.00	102		1140	Linen, wire uncharged, slow rate of decay
30	18	38		56		1.000		140			Linen, wire uncharged, slow rate of decay
31	18	41		134			101	110			Linen, wire uncharged, after 24 hours 10 per cent. left
32	14		45			94	112	165			Linen, wire uncharged, after 6 hours 8 per cent. left
*33	8	26				89					Linen, wire uncharged, raining
34						129				1200	Linen, wire uncharged, slow rate of decay

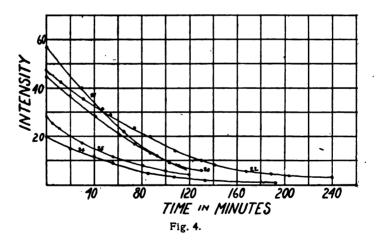
#### TABLE I.—Continued.

Intensity in Per Cent.

No.	80	60	50	40	30	25	20	18.5	6.3	3.1	Remarks.
45	18	37	48	60	75	84	97	120	156		Linen, wire uncharged
46	22	37	45	54	69	78	92	114			Linen, wire uncharged
47	18	39	52	64	81	90	104	130			Linen, wire uncharged
48	22	41	51	62	75	82	91	112	146		Linen, wire uncharged
49	8	22	35	49	67	78	93	132			Linen, wire uncharged, slow rate of leak
50	20	35	43	54	66	76	86	108			Linen, wire charged I hour
51	14	30	40	52	67	76	90	120			Linen, wire charged 2.5 hrs., after 19 hrs. 2.3 per cent. left
#42a	12	27	38	52	68	80	95	116	·		This curve is the mean of curves marked *

wire, time of exposure and duration of activity. The figures in the intensity columns represent the times taken for the activity to decay to various percentages of the maximum. The time taken to fall to 50 per cent. we will call the period of decay.

A glance at the curves shows at once the extreme irregularity both in shape and period of decay. From Table I. under 50 per cent. we see periods ranging all the way from 36 minutes to 79



minutes. Only one curve 42, Fig. 7, is truly exponential over any great length of time, this having a period of about 38 to 39 minutes.

A study of these curves brings out the fact that they can mostly be grouped under three heads :



No. 6.1

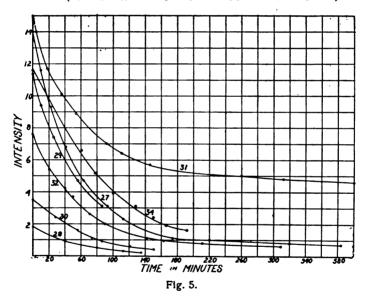
1. Exponential, or approximately so, and capable of being represented by an equation of the familiar form,

$$I_{\iota} = I_{0} e^{-\lambda t}.$$

2. Curves like 48 and 50, consisting of a convex upward part at first, and then of an approximately exponential part having a period of about 30 minutes.

3. Those having at first a more rapid decay, and afterwards a slower one extending over several hours, the period of this last being about eleven hours.

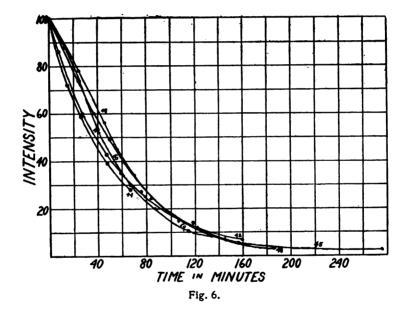
In examining the periods as expressed in Table I., it is seen that eleven curves (2, 12, 14, 16, 19, 25, 28, 33, 41, 42, 43, 44) can be



classed under head (1) as being approximately exponential and having a period of 36-40 minutes. None of these curves shows any appreciable amount of the slow rate of decay. Curve 42a represents the mean of these curves and it is nearly identical with 42 (the exponential one), having a period of 38 minutes.

The agreement between these curves is certainly not accidental and represents a simple and common rate of decay. One cannot identify it with any of the simple rates of decay of the active deposits from the radioactive substances. It may be, and probably is, a mixture of radium B and radium C in invariable proportions. It is, however, worthy of note that actinium A has a period of about 36 minutes.

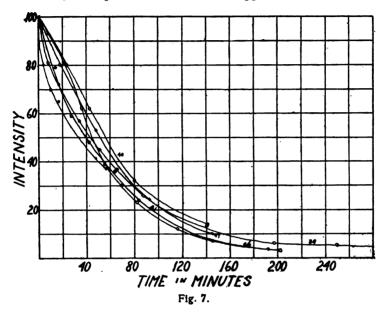
The curves under head (2) are very similar in general shape to the curve of decay of the excited activity due to radium (leaving out the first rapid stage), and are probably caused in part by the



radium emanation present in the air. The exponential part of these, having a period of decay of about 30 minutes, shows very good agreement with radium C. These curves were obtained for both the charged and uncharged wire and in the two cases represent the maximum amount of activity collected during the entire series



On some days the uncharged wire was first rubbed over with a piece of linen, then charged negatively for a certain time and the two active deposits tested. Under these conditions whenever the slow rate of decay was present in one, it also appeared in the other. It

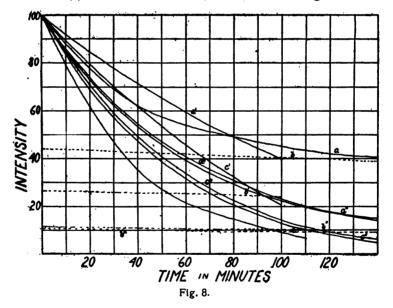


could be obtained for a short exposure of the wire as well as for a long one, though naturally in the latter case under the same conditions the amount was greater than in the former.

No.	100	50	25	12.5	6.3	
13 & 29	0	37	72	101	129	الى
26	0	44	90	122		ſ
32	0	39	75	105	136	<i>d1</i>
34	0	54	104	141	176	ſ
31	0	28	54	86	111	c
51	0	37	67	97	128	f"
39	0	41	82	111	136	fil
23	0	54	92		1	d

TABLE II.

If this slow rate of decay is due to thorium A and the amount of it be known at any time after the start, the amount at any other time can be easily calculated from the equation  $I_t = I_0 e^{-\lambda t}$ , representing the decay of thorium A. This rate of decay can then be subtracted from the actual observed rate, and the net decay obtained. I have done this for nine curves, which show to a marked degree the amount of thorium A present, and the results are shown in Figs. 8 and 9. For example, curve (a), Fig. 8, represents the actual curve observed; curve (b) that of the thorium A present, while curve (c) shows the net decay. It is interesting to note that



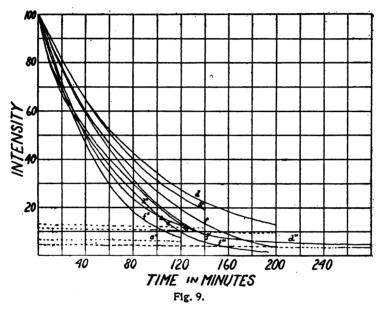
this curve (c) is very approximately exponential and has a period of from 26 to 28 minutes. It is somewhat difficult to estimate with accuracy the amount of thorium A present, which will probably account for the departure of the curve from the exponential towards the bottom, where the amount of thorium A is more than comparable with the remainder. The upper part of the curve is therefore

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No. 6.]

curves varies greatly in proportionate amount. For the sake of comparison, the results are collected in Table II., which is of the



same character as Table I. The periods are given under column headed 50. It will be noticed on examination of this table, that, although the periods for the first part of the curve differ considerably, towards the end they all approach about 30 minutes. With the exception of curve (c) they are all complex, but show the presence of radium C. Two of them (f) and (c') show the presence of a slower rate of decay.

Table	III.
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No. of Curve.	Periods.	No. of Curve.	Periods.
42	39, 40	34	54, 39
40	52, 36	51	38, 30
45	56, 41, 36	39	28, 54
31	28	4	51, 40, 31
13 and 29	33, 29	8	42, 38
32	34, 29		•

periods calculated. The results are shown in Table III., which gives the component periods as far as could be obtained. With one or two exceptions these can be put in three classes, viz :

1. Period 28-31 minutes, due to radium C.

2. Period 37-40 minutes, due to the same cause as those II curves already discussed, probably a mixture of radium B and C, possibly in some cases actinium A.

3. Period 52-56 minutes, cause not apparent. (Thorium B has a period of about this amount.)

In conclusion, I think it can be safely stated, that the curves of decay for the excited activity of the atmosphere, where large quantities of smoke particles are present, will show many irregularities, but may be analyzed into component parts, which agree with the rates of decay of the excited activities of the radioactive substances, radium, thorium and possibly actinium.

Also the radioactivity under these conditions can to a large extent be collected on an uncharged wire, being carried there by the settling of the smoke particles. The activity due to the radium is always present, while that caused by the thorium is much more variable, and often absent, or at least in inappreciable quantities.

UNIVERSITY OF CINCINNATI, January, 1908.



# PROCEEDINGS

#### OF THE

# American Physical Society.

# THEORIES OF THE COLOR OF THE SKY.<sup>1</sup>

# BY EDWARD L. NICHOLS.

I N asking your attention to-day, even briefly, to the consideration of the present state of our knowledge concerning the causes of the color of the sky it may be truly said that I am inviting you to leave the thronged thoroughfares of our science for some quiet side street where there is little going on and you may even suspect that I am coaxing you into some blind alley, the inhabitants of which belong to the dead past. Nevertheless, the problem is not a simple one. It cannot be considered as settled or likely to be soon completely solved.

#### **Review of Existing Theories.**

It is true that the theory suggested by Brücke,<sup>3</sup> appears to many minds conclusive and all sufficient. The famous demonstrations of Tyndall<sup>3</sup> and the masterly theoretical work of Rayleigh<sup>4</sup> may be said to have established Brücke's view that the color of the sky is that of a turbid medium. More recent experimental work has been in a general way confirmatory of this theory.

At the same time it should not be forgotten that other explanations of the color of the sky have been offered. Clausius <sup>6</sup> in a classical paper, has shown that the color of the sky is deducible on theoretical grounds from the assumption of the existence of minute vesicles or water bubbles suspended in the air. Hagenbach <sup>6</sup> has pointed to the reflection from surfaces of moving bodies of air as the probable cause of the blueness of the sky. Spring <sup>1</sup> has called attention to the fact that oxygen, ozone, water and hydro-

<sup>1</sup>Presidential address delivered at the New York meeting of the Physical Society, February 29, 1908.

<sup>2</sup> Brücke, Poggendorff 's Annalen, LXXXVIII., p. 363, 1852.

<sup>8</sup> Tyndall, Proc. Royal Society, XVII., p. 223, 1868 ; also Phil. Mag. (4), XXXVII., p. 388.

<sup>4</sup> Rayleigh, Phil. Mag. (4), XLI., pp. 107 and 447, 1871.

<sup>5</sup>Clausius, Pogg. Annalen, LXXVI., p. 161; LXXXIV., p. 449, 1849.

<sup>6</sup>Hagenbach, Pogg. Annalen, CXLVII., p. 77, 1872.

<sup>7</sup> Spring, Bulletins de l'Academie Belge (3), XXXVI., p. 504.

gen peroxide, all of which are constituents of our atmosphere are blue, and that they are present in sufficient quantity to amply account for the preponderance of the shorter wave-lengths in the light which reaches us from the atmosphere. Lallemand<sup>1</sup> and also Hartley<sup>2</sup> have sought for an explanation in the fluorescence of the ozone of the upper atmosphere, and finally subjective color<sup>3</sup> has been advanced as a possible explanation.

Of these various theories only that of Clausius can be discarded without further consideration. That the atmosphere is a turbid medium we have overwhelming experimental evidence but that this turbidity is in itself the sole source of color does not necessarily follow. It has been a characteristic of nearly all the literature of this subject that each author has emphasized some one explanation to the exclusion of all others, although Pernter<sup>4</sup> who is one of the most strenuous advocates of the theory of turbidity, is inclined to consider the fluorescence of ozone as a possible additional factor. Jansen<sup>6</sup> alone, so far as I know, in an interesting summary of the literature of the subject treats the color of the sky as due to the combination of a number of factors.

We may state the case as follows:

1. The turbidity of the atmosphere would of itself give us a blue sky, but the ideal medium of Rayleigh would afford a distribution of intensities to which the actual sky rarely if ever corresponds.

2. Even were the atmosphere free from particles of dust, condensed water vapor or other extraneous matter it would not, according to Rayleigh's latest paper, be optically empty, to use the term employed by Tyndall, but would be blue by virtue of reflections from the molecules of the air itself.

3. If there were no other source of blueness, the color of the air, according to Spring, would give us a blue sky by virtue of the selective absorption-color of various of its constituents. The objections to the adoption of this as a factor are obvious and are regarded by many writers as insuperable but their arguments are not in my opinion conclusive.

4. Reflection from surfaces in a troubled atmosphere as pointed out by Hagenbach, would give us light from the sky increasing in intensity relatively to sunlight in proportion to the square of the wave-length.

5. Fluorescence as a factor of blueness of the sky cannot be definitely considered at the present time for lack of experimental data concerning it.

6. As regards the subjective or physiological factor it may be said that were there no other cause the sky would undoubtedly appear blue; for we still see it blue where measurements with the spectrophotometer indicate a composition relatively much weaker in the shorter wave-lengths of the spectrum than the *average* composition of sunlight. In the present paper I shall, however, consider only the objective factors.

The problem of the color of the sky resolves itself then into a determination of the relative importance of these various factors, the existence of all of which with the possible exception of fluorescence must be regarded as experimentally established. Such an analysis is unfortunately a difficult matter on account of the complexity of the phenomena and because the observer cannot create his conditions nor hold them constant.

The phenomena of aerial polarization indicate beyond any doubt the turbidity of the air as one source of the blueness of the sky. In the case of the ideal turbid medium of Rayleigh, in which all the particles are small as compared with the wave-length of light, the composition of the diffused light, as is well known, is such that the ratio of the intensity of the reflected ray to that of the incident ray varies inversely as the fourth power of the wave-length. This would give us a sky about twelve times as bright in the extreme violet as in the red, as compared with sun-Rayleigh's analysis may be said to have found complete verificalight. tion in the experimental study of artificial turbid media, particularly in the studies of the colors of the steam jet by Bock.<sup>1</sup> Spectrophotometric measurements of the sky itself have, however, led to widely varying re-Zettwuch,<sup>3</sup> who made many measurements of the sky at Rome, sults. calls especial attention to its extreme variability. Crova,<sup>3</sup> who has made more measurements of this sort than any other investigator with whose work I am acquainted, obtained, in the course of measurements at Montpellier extending over more than two years, relations for the variation of intensity with wave-length in which the exponential constant ranged from 1.61 to 6.44. Crova's measurements unfortunately extend only through the brighter parts of the spectrum from  $.635 \,\mu$  to  $.510 \,\mu$ ; the extreme red and the violet being omitted. If, however, we are to accept his exponential coefficients as even approximately correct, we shall have an admis show assumed for the blind of the about them that at surbidiar

#### Some Determinations with the Spectrophotometer.

Certain measurements with a portable spectrophotometer, which I have undertaken in various localities, during a recent vacation may be of interest as indicating the nature of the phenomena with which we have to deal even if they afford insufficient data for the solution of the general question.

Comparisons of the light from the sky with direct sunlight by means of the spectrophotometer are chiefly interesting as a means of determining the relation between actual skies and the ideal sky imagined by Rayleigh. For other purposes such measurements are of little value on account of the variable quality of sunlight after passage through the earth's atmosphere, and because the sky receives a portion of its illumination from light reflected from clouds and from the surface of the earth ; and further because of absorption which the blue light from the sky suffers from the turbid medium itself. To indicate the variations in the quality of sunlight which are encountered in making direct comparisons of sky and sun I may say that the range in the relative intensity of sunlight when compared with the acetylene flame employed as a standard source in my measurements was between 9.9 at Brienz, Switzerland, on August 19, 1907, and 10.2 at Andermatt on August 9 of that year, on the one hand, and 3.57 at Brienz on August 13, where these quantities express the intensity of the sun's spectrum in the violet  $(.418 \,\mu)$  as compared with the spectrum of the standard flame. Both spectra were taken of equal intensity in the red at .725 #.

Measurements of artificial turbid media are not open to this difficulty. Bock, whose steam jet, made turbid by the action of hydrochloric acid gas, seems to have afforded the most favorable conditions for investigation, found the following relative intensities, the intensity in the red being taken as unity :

Red	1.00
Yellow	1.52
Green	2.89
Blue	4.35
Violet	9.81

Rayleigh's formula for the ideal medium gives for the corresponding regions :

Red	1.00
Yellow	1.98
Green	2.82
Blue	4.92
17:-1-4	0 60

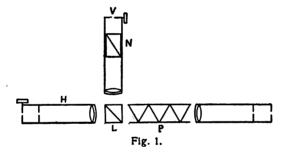


No. 6.7

red, to be as 5.7, 8.7, 6.5, 5.2, 4.3. Of these only one shows an approach to the ideal value.

In comparing the spectrum of the skylight with that of an artificial standard, the flame sources hitherto employed, namely, the petroleum flame, by Vogel; the Carcel flame, by Crova; and the Hefner flame, by Frl. Köttgen; are too weak in the violet to admit of satisfactory measurements in that region. The acetylene flame which I have employed in my recent experiments is better in this respect, being relatively about three times as bright in the violet as the sources previously employed, and I have attempted to cover a much wider range than earlier observers, namely, from .725  $\mu$  in the red to .390  $\mu$  in the extreme violet. It is in these regions at the extreme ends of the visible spectrum, hitherto uncovered by spectrophotometric observations, that some of the most interesting and striking variations of the light from the sky occur.

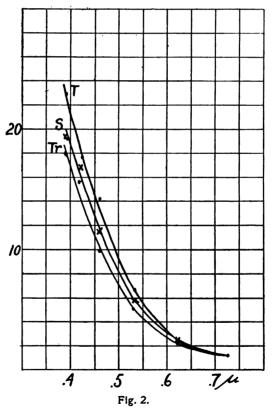
The instrument employed was planned with special reference to portability. It consists essentially of a simplified Lummer-Brodhun spectrophotometer with a vertical collimator V, containing a nicol N, and a horizontal collimator H, as shown in Fig. 1. For the single prism of the



original instrument a set of direct vision prisms P is substituted. The comparison source is a small flat acetylene flame surrounded with a hooded chimney of black metal. In front of the flame is a diaphragm with an aperture of 2 mm. diameter so that only the central portions of the flame send light to the slit. About 3 cm. in front of this diaphragm is a circular screen of milk glass which within the limits of the visible spectrum exhibits no marked selective absorption. This lamp is mounted in front of the horizontal slit of the spectrophotometer and access of all light from other sources is excluded by screens.

The acetylene lamp is supplied from a small portable generator and a light rubber bag is used as a storage reservoir and to equalize the pressure of the gas supplied to the flame. Such a comparison source does not realize the conditions as to uniformity of intensity which can be obtained in the laboratory but the variations were rarely troublesome and indeed the degree of constancy was quite sufficient for the purposes of studying so variable a spectrum as that which we obtain from the sky.

Numerous measurements of the spectrum of the sky in various localities by means of this apparatus showed, in general, far greater relative intensities of the longer wave-lengths than one would expect from the theory of Rayleigh. Direct comparisons of skylight and sunlight made by substituting for the standard flame a screen smoked with magnesium oxide and exposed to the sun's direct rays, with adequate precautions to prevent





To determine definitely and quantitatively the relative importance of these and other possible factors is a matter of great difficulty; but the study of numerous curves obtained under different conditions throws some light upon the question. It was found that curves taken at dawn and in the twilight after sunset showed a much greater relative preponderance of blue than those taken during the day. These curves moreover were all of the same type and in close agreement with each other as regards the distribution of intensities. In Fig. 2 a group of such curves is given, all reduced for comparison to equal intensity in the extreme red.

While it is impossible to make a direct comparison between such spectra observed at dawn or twilight with the spectrum of the rays by means of which the sky overhead is illuminated, an indirect approximate estimate may be made by means of comparisons made during the day immediately following or immediately preceding, as the case may be, of sky and lamp and then of sky and sun. From several such computations it appears that the skylight curves at dawn and twilight not only show far greater constancy of type than do mid-day measurements, but also a fair approximation to the *ideal* sky. I found for example from measurements made at Sterzing (Tyrol) on July 18 at 4:55 A. M. (before sunrise) and the comparison of these with measurements on the same day between 8 and 9 A. M., in which ratios between sky and lamp on the one hand and sky and sun on the other were obtained, that the probable early morning sky/sun ratio was 8.9 at wave-length  $.418 \mu$  both being reduced to unity at  $.725 \mu$ . The ratio for the ideal sky after Rayleigh's formula for these wave-lengths is 0.3.

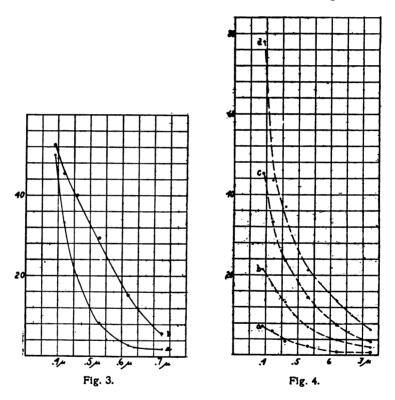
Since these dawn-twilight skies by fair weather show but little variation as to composition I have taken the average of the data at my disposal and have called the resulting curve the *typical dawn curve*. For convenience this is arbitrarily given an intensity of unity in the extreme red  $(.725 \mu)$  and other ordinates express the ratio of the skylight to the light from the flame, wave-length for wave-length, throughout the spectrum. The characteristic difference between the typical dawn curve, or any individual dawn curve by fine weather, since these are found to agree closely in composition, and the spectrum of the sky in the middle of the day referred to the same comparison source is shown in Fig. 3. It will be seen that while the skylight taken as a whole is greatly increased in intensity the actual intensity of the blue and the violet is much less affected than are the longer wave-lengths.

The gradual change in the quantity and character of the light from the sky as the sun rises in the heavens is shown in Fig. 4, which contains curves obtained at Sterzing (Tyrol) at 4:45 A. M., before sunrise (a), at 5:40, soon after sunrise (b), at 7:00 (c) and at 8:25 A. M. respectively, on a cloudless and unusually clear morning.

This relation of curves taken after sunrise, to the typical dawn curve is more obvious if we plot the ratios of the curves to be compared for each wave-length of the spectrum. The results for curves b, c and d of Fig. 4 are given in Fig. 5.

These curves of ratios are significant because they repeat themselves persistently as to type, although with certain systematic variations, in the case of numerous measurements taken in various localities.

In fine weather, especially in summer, the moisture of the atmosphere tends to condense and to form masses of sunlit cloud which gather in the



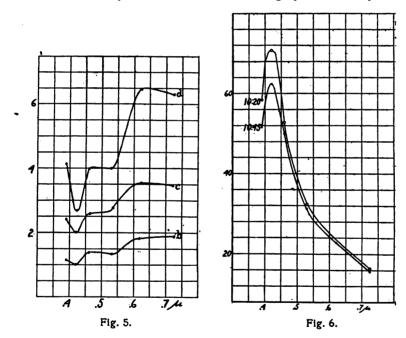
middle of the day and disappear towards sunset. The sky/acetylene curve then takes on another distinctive form well illustrated in Fig. 6. The two curves there shown were taken at Sterzing about two hours after the completion of the set of morning measurements plotted in Fig. 4.

Fig. 7 shows the culmination of this effect in the curve for 1:30 P. M. obtained from a very bright sky with masses of cumuli, its persistence with much reduced intensities at 5:50 P. M. and its almost entire disappearance at 6:45 P. M. The two curves for 7:20 and 7:40 P. M.

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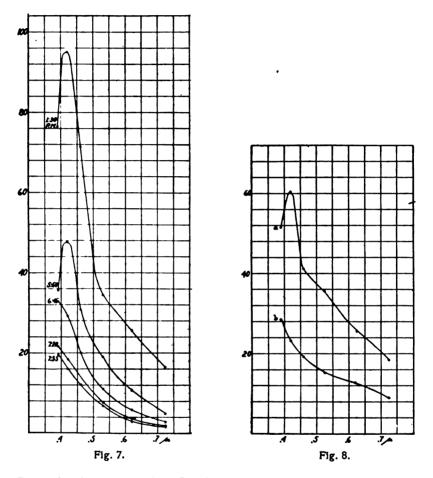
about sunset — show complete return to the early morning type. This form of curve is especially characteristic of summer weather in the mountains and the droop towards the ultra-violet was most pronounced in high localities, as at Andermatt, Samaden (Engadine), on the Rhone Glacier and on the Brienzer Rothhorn. It occurred occasionally, but in less fully developed form in the winter skies of Algeria and Sicily.

The study of the sky, on foggy mornings when the air was filled with sunlit mist through which the sun and the blue sky were dimly visible yielded other and slightly different curves, always similar in form and characteristic of this state of the atmosphere (Fig. 8, a). Overcast skies gave distinctive forms (Fig. 8, b), notable for their general resemblance to certain curves obtained from the clear sky. The relations of these various types will be considered in a forth-coming paper. They are mentioned here only because of a certain bearing upon the theory.



There is good reason to think certain features of the curves of ratios illustrated in Fig. 5 are due to the illumination of the sky by light reflected from the earth. The maximum at  $.625 \mu$  and the minimum at  $.525 \mu$  occur in all curves taken when the landscape is under direct sunlight. They are most marked in measurements made at stations in the open country, as at Taormina, Trafoi and Sterzing, less prominent in the winter skies at Biskra and Palermo and least of all in observations

at Vienna where the sky was always seen through a pall of smoke. Mist and over-cast skies, of which the curves in Fig. 8 (a and b) are typical, are devoid of these two selective features, as will be seen from the curves of ratios given in Fig. 9. Two of these examples, B and



Z, are for fog, measured at Bebek on the Bosphorus and at Zell am See in Austria, and two, V and T, for clouded skies at Vienna and Taormina respectively when the landscape was untouched by sunlight. The absence of the features under consideration, and which are so obvious in Fig. 5, will be noted. These features are also missing in measurements taken at sea during bright weather. The fact that the region  $.525 \mu$ corresponds to one of the strongest absorption bands of the spectrum of light transmitted by chlorophyl and  $.625 \mu$  to the brighest portion of

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that spectrum may be taken to indicate that presence of foliage modifies to a measurable extent the character of the light from the sky. In other

words we have, when the landscape is sunlit, a weak chlorophyl spectrum superimposed upon the true spectrum of the light from the sky !

No. 6.1

We have, therefore, in light reflected from the earth one of the causes of the deviation of many skies from the distribution of intensities to be expected from an ideal turbid medium illuminated only by direct sunlight. Reflection from cloud masses is often another source of illumination and by means of the spectrophotometer the selective character of such light, which closely resembles that from fog or mist, can readily be determined.

# INFERENCES FROM THE POLARIZATION OF THE SKY.

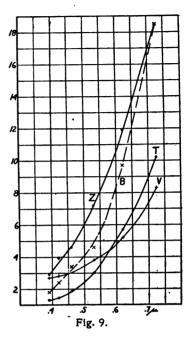
Some of the strongest arguments for regarding the atmosphere as a turbid medium are derived from the study

of the character of the polarization of skylight.

The phenomena described by Tyndall as the result of his study of artificial turbid media and his application of the same to the sky are confirmed and in a manner explained by observations with the spectrophotometer. Pernter<sup>1</sup> who made extended observations upon the light diffused by alcoholic solutions of mastic gum found the degree of polarization of the red, green and blue to vary in a remarkable manner according to the color of the emulsion. He found in general the light emitted at right angles to the illuminating beam to be less polarized the whiter the appearance of the medium — which is also true of the sky. For blue emulsions the green showed the greatest polarization, then the blue and then the red. For whiter emulsions the red was most strongly polarized and the effect diminished toward the violet. He found the same to be true of blue and whitish skies respectively.

In comparisons of the distribution of polarization in the spectrum of skylight from the zenith, taking the ratio of the brightness of the component polarized in the sun's vertical plane to that at right angles to the same, I obtained the results shown graphically in Fig. 10.

<sup>1</sup> Pernter, l. c.



It will be seen from the figure that the polarization of the sky is sometimes:

(a) Greatest in the violet.

(b) Greater in the green, yellow or blue than in the red or violet.

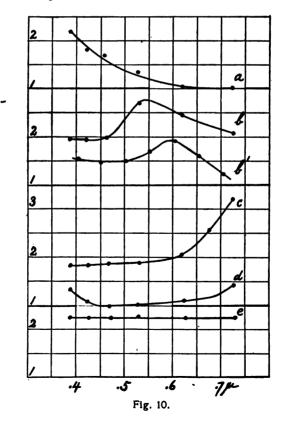
(c) Greatest in the red.

(d) Least in the middle of the spectrum.

(e) Nearly uniform throughout the visible spectrum.

The ideal turbid medium of Rayleigh would give complete polarization of all wave-lengths at an angle of 90°. If, with Pernter,<sup>1</sup> we consider that a medium may have this character for longer waves and yet reflect unpolarized light of shorter wave-length, the various cases noted above may be accounted for as follows:

(a) When the polarization increases towards the violet as in the ob-



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ing particles. Since light from the latter will be relatively weaker in the violet the percentage of polarized light will be greatest in that region and will diminish as we pass toward the red. The distribution of intensities in such a sky will obviously show greater relative strength at the red end of the spectrum than would the ideal sky.

(b) Observations made at Salzburg, July 5, 1907 (Fig. 10, b), also at sea on February 9 (Fig. 10, b'). The medium from which the light is derived may be a mixture of the *ideal* medium, with a medium ideal for green but not for violet, together with particles reflecting unpolarized light throughout the spectrum.

(c) Observations made at Chur on August 4 (Fig. 10, c). The *ideal* medium may be mixed with a medium ideal for red but not for green and the shorter wave-lengths, and also with coarser particles.

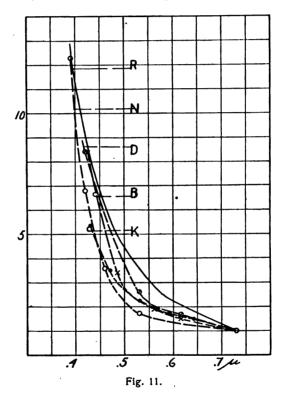
(d) Observations made at Biskra on February 24 (Fig. 10, d). It is possible that we have in this example a combination of the conditions producing a and c. Light from a region or layer of the atmosphere giving preponderance of polarization in the red may be considered as mingled with light from regions giving polarization chiefly in the violet.

(c) Case c offers greater difficulties. It might of course indicate an ideal sky but none of the skies for which this condition as to polarization was observed approached the ideal in relative intensity in the violet. The skies for which a uniform distribution of polarization was actually obtained were, indeed, very far from the ideal as to distribution of intensities. We may imagine as one of several combinations of circumstances which would produce this condition, a sky consisting of the ideal medium mingled with a coarser medium reflecting unpolarized light as in case (a) and that the preponderance of the polarized violet is removed by absorption of the light diffused by the ideal medium in passing through extended regions filled with the same. The change of composition would be analogous to that observed in fluorescent solutions of considerable concentration, where there is always a shift of the fluorescence band toward the infra-red. One may also imagine other combinations where the effects described under b, c and d happen to balance each other giving uniformity throughout the spectrum. Skies giving polarization curves of the types b. b' and c might obviously be expected to show the phenomenon designated by Tyndall as residual blue.

# EVIDENCE CONCERNING OTHER FACTORS IN THE PRODUCTION OF SKYLIGHT.

As has already been pointed out, the blue color of the air itself and a blue or violet due to fluorescence of ozone or other components of the atmosphere are to be regarded as possible factors in the production of the color of the sky. Data upon this subject are very incomplete and not

altogether conclusive. It is significant however that Crova in certain of his measurements, referred to in a previous paragraph, ob'ained an exponent much higher than that demanded by Rayleigh's theory. I find furthermore that all available measurements which give a near approach to the proper relation between the extreme red and the violet of the spectrum, namely, an increase of intensity of the violet which is inversely



proportional to the fourth power of the wave-length, give values relatively much too small in the middle of the spectrum. This is true of the twilight and dawn curves obtained from my own measurements and likewise of the only set of measurements made by Bock in which the intensity of the violet approached the value corresponding to that of the ideal sky. While Miss Köttgen made no direct comparisons of sky and sun she measured both skylight and sunlight in terms of the Hefner lamp. Making use of her data one can compute the sky/sun ratios under the as-

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curve to have the same peculiarity, that is to say, like the curve plotted from Bock's data and like my own curves there is marked relative weakness throughout the middle of the spectrum. This peculiarity could be readily explained by assuming a turbid medium containing particles too large to give the ideal sky but having a distinct blue color of its own due either to absorption, in accordance with Spring's theory, or it might be due to fluorescence in the violet end of the spectrum or to absorption and fluorescence combined. The nature of the departure of these curves from the ideal form, which is illustrated in Fig. 11, is quite consistent with and indeed explanatory of the occasional high values of the exponential factor found by Crova. In Fig. 11, R is the curve for the ideal turbid medium, N is one of the very few cases in which I obtained a relation between red and violet in accord with Rayleigh's theory. D is from my typical dawn curve, B and K are from the data of Bock and Köttgen respectively.

#### SUMMARY.

It has been my endeavor in this paper to show :

1. That while there is good reason for regarding the sky as a turbid medium, the experimental study of the spectrum of skylight affords evidence of a distribution of intensities which cannot be altogether accounted for by the assumption of an atmosphere conforming to Rayleigh's formula nor of a turbid medium containing coarser particles.

2. That the illumination of the atmosphere by selectively reflected light from the surface of the earth and from cloud masses and mist modifies the character of the light from the sky to an extent which while perhaps not readily discernible with the unaided eye is definite and unmistakable when the sky is studied with the spectrophotometer.

3. That the deviation of the observed distribution of intensities recorded by several investigators indicates a blue absorption color of the air or, since the preponderance in the violet appears to be variable in amount, the existence of fluorescence of some unstable factor of the atmosphere such as ozone or both.

PHYSICAL LABORATORY OF CORNELL UNIVERSITY, February, 1908.

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# MINUTES OF THE FORTY-FIRST MEETING.

THE spring meeting of the Physical Society was held in Washington, D. C., on Friday, April 24, and Saturday, April 25, 1908. President E. L. Nichols presided.

The Friday session was held at the Cosmos Club, and the Saturday sessions at the Bureau of Standards. At the close of the Saturday afternoon session, upon invitation of the director, the Society visited the new Geophysical Laboratory of the Carnegie Institution.

The secretary reported that the informal mail ballot on the question of increasing the annual dues showed 255 votes in favor of the increase and 32 against. Acting upon recommendation by the Council the Society thereupon voted to amend Article II. of the By-Laws by striking out the word "five" and inserting in its stead the word "six," the effect of the amendment being to increase the annual dues of members to six dollars.

The attention of the Physical Society was called to an International Electrical Congress which it is proposed to hold in London next October. It was suggested that the questions involved be fully discussed, previous to the meeting, by a joint committee representing the American Physical Society, the American Institute of Electrical Engineers, and the Electro-Chemical Society, in order that the delegates to be appointed by this Government should have the benefit of the opinions reached by American investigators who have been engaged in a study of the standard cell and the silver coulometer, as well as those who havé given especial attention to the other questions involved in the selection and definition of the fundamental electrical units.

On motion the president was authorized to appoint such a committee, and Messrs. Bedell, Carhart, Guthe, Hulett, Rosa, Elihu Thomson, Webster, and Wolff were named by the president as members of the committee.

The following papers were presented :

What Proportion of the Earth's Magnetic Force in the United States is Due to a Potential? L. A. BAUER.

The Effect of Wave Form upon Magnetic Hysteresis. MORTON G. LLOYD.

The Influence of Terminal Apparatus on Telephonic Transmission. LOUIS COHEN.

What is the Most Important Portion of a Thermoelement? WALTER P. WHITE.

A Study of Photo-active Cells Containing a Fluorescent Electrolyte. PERCY HODGE.

A Photometer for the Measurement of the Rate of Decay of Gas Phosphorescence. C. C. TROWBRIDGE.

A Spectrophotometric Study of Kathodo-luminescence. EDWARD L. NICHOLS and ERNEST MERRITT.

A Study of the Thermo-luminescence of Balmain's Paint. (By title.) C. A. PIERCE.

Variation of the Penetrating Radiation. W. W. STRONG.

Specific Heat of some Calcium Chloride Solutions. H. C. DICKIN-SON and E. F. MUELLER.

The Application of the Ionization from Hot Bodies to Thermometric Work at High Temperatures. O. W. RICHARDSON.

Note on the Joule-Thomson Effect in Superheated Steam. H. N. DAVIS. New Groups of Residual Rays in the Long Wave Spectrum. Preliminary Report. E. F. NICHOLS and W. S. Day.

Resonance Spectra of Sodium Vapor. R. W. WOOD.

Interference of Light in Laminæ of Chlorate of Potash. R. W. WOOD. Experiments with the Lippmann Color Photograph. H. E. IVES.

The Relation of Light of Very Short Wave-length to some Vacuum Tube Phenomena. THEODORE LYMAN.

Additional Observations on the Selective Reflection of Salts of Oxygen Acids. LEIGHTON B. MORSE.

Optical Properties of Colloidal Solutions and Turbid Media in the Infra-red. B. J. SPENCE.

On Diffuse Reflection of Infra-red Energy. A. TROWBRIDGE.

Fundamental Questions Involved in the Selection of Definitions and Specifications of Electrical Units. S. W. STRATTON.

The Relative Merits of the Coulometer and Standard Cell from the Standpoint of their Use in Fixing the Values of the Fundamental Electrical Units. F. A. WOLFF.

The Infra-red Absorption and Reflection of Collodion. A. TROWBRIDGE.

The Absorption Spectrum of Neodymium in Mixed Solvents. JOHN A. ANDERSON.

The Remarkable Optical Properties of Carborundum. L. E. JEWELL. Specific Heats at High Temperatures. (By title.) WALTER P. WHITE. Preliminary Note on the Effect of Low Temperature on Optical Rotation. (By title.) F. A. MOLBY.

An Electrodeless Method for Measuring the Conductivity of Electrolytes. LOUIS COHEN.

Note on the Radioactivity of Ordinary Metals and on the Penetrating Radiation from the Earth. (By title.) J. C. MCLENNAN.

The Absorption and Reflecting Power of Calcite and Aragonite in the Infra-red as Dependent upon the Plane of Polarization of the Incident Rays. (By title.) R. E. NYSWANDER.

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# A New Form of Interferometer.<sup>1</sup> By C. W. Chamberlain.

THIS instrument is provided with three carriages, any one of which may be moved over a single bed plate by means of a slow motion screw. On the central carriage are mounted two  $8 \times 25 \times 80$  millimeters plane parallel plates in contact with each other. Their outer faces are covered for 55 millimeters of their length with reflecting metallic surfaces, while the inner surface of one plate is provided for 25 millimeters or more of its length with a semi-transparent metallic film. A thin film of Canada balsam may be placed between the plates. On the end carriages are mounted mirrors 10  $\times$  25  $\times$  70 millimeters with their reflecting surfaces facing the central plates and making equal but variable angles with them.

Light incident upon the semi-transparent film is reflected and transmitted to the end mirrors and then reflected many times between them and the silvered portions of the central plates. The reflected and transmitted beams are finally returned over their paths to the semi-transparent film where they are partly transmitted and reflected to the eye and are recombined and made to interfere.

By changing the angle between the end mirrors and the central plates interference fringes from the first to the twentieth order may be made to appear. The instrument is readily adjusted to bring fringes of several different orders into the field of view at the same time.

The following relationship exists between the movement of the central carriage and the number of interference fringes seen to cross the field of view.

Let  $\beta$  = angle between the central plates and the end mirrors.

- x = movement of the central plates in a direction normal to their surfaces.
- n = number of the order of the fringes, i. e., n gives the number of times the ray is reflected from an end mirror.
- $f_n =$  number of fringes that pass the field of view when the *n*th order of fringes is used.
- $\lambda$  = wave-length of light employed.

$$x = \frac{f_n \lambda}{4 \cos \beta \cos n\beta} \left\{ \frac{I}{\cos n\beta \cos (n-1)\beta} + \frac{I}{\cos (n-1)\beta \cos (n-2)\beta} + \frac{I}{\cos (n-2)\beta \cos (n-3)\beta} + \frac{I}{\cos \beta} + \frac{I}{\cos \beta} \right\}.$$

<sup>1</sup>Abstract of a paper presented at the New York meeting of the Physical Society. February 29, 1908.

# The Relation of Light of Very Short Wave-Length to Some Vacuum Tube Phenomena.<sup>1</sup>

#### BY THEODORE LYMAN.

S CHUMANN has observed that the radiation which comes from the neighborhood of the cathode in a vacuum tube is particularly rich in light of very short wave-length. The writer began the present investigation for the purpose of ascertaining if these most refrangible rays were confined entirely to the region near the negative electrode.

As a result of these experiments it may be stated that the positions of the sources of light of very short wave-lengths coincide with the places of luminosity in the vacuum tube. Thus the ozone test<sup>2</sup> shows some slight effect very near the cathode, little effect in the Crookes dark space, a maximum effect at the head of the negative glow, no effect in the Faraday dark space, a feeble effect throughout the length of the positive column, and a fairly well marked effect near the anode.

The latter half of the paper relates to the part played by light of very short wave-length in producing ionization within a discharge tube. That some kind of radiation acts to increase the conductivity in the electric discharge at low pressures has been proved by J. J. Thomson, and the effect has been attributed by him to the influence of the "Entladungs-strahlen" discovered by Wiedemann. One of the objects of the present paper is to show that in all probability the active agent in producing ionization is not a new form of radiation but light of wave-lengths shorte than  $\lambda$  1,800.

The subject naturally leads to an inquiry into the nature of Entladungsstrahlen themselves. The writer points out that the phenomena attributed to this new agency are complicated by the action of light of very short wave-length to a far greater extent than had previously been supposed.

JEFFERSON PHYSICAL LABORATORY, HARVARD UNIVERSITY, April 22, 1908.

A Photometer for the Measurement of the Rate of Decay of Gas Phosphorescence.<sup>1</sup>

#### By C. C. TROWBRIDGE.

THE author described a new form of photometer designed for the purpose of measuring the rate of decay of luminosity of a phosphorescent gas. The photometer consists of a track 3.5 meters long, made of two brass rods under tension. On the track an electrically concan be moved away from a screen placed close to a tube containing the phosphorescent gas to points A, B, C, etc., on the photometer track. The illumination on the screen from the standard light is thus directly compared with the luminosity of the gas, and comparisons are made with the standard light at A, B, C, etc., as the gas fades. When a comparison is registered at A, the time recording key also releases the carriage carrying the standard light so that it moves by means of weights until stopped at B, ready for the next comparison. Seven readings can be

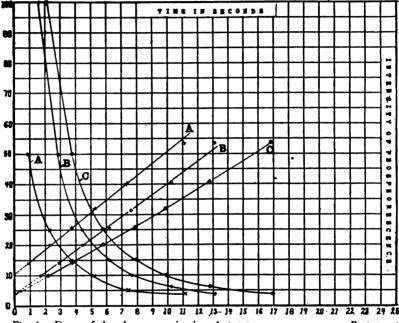


Fig. 1. Decay of phosphorescence in air; A at 0.14 mm. gas pressure, B at 0.227 mm. pressure, C at 0.222 mm. pressure. Curves B and C show different rates of decay at approximately the same gas pressure, due to changes in the condition of the rarefied gas.

made within ten seconds, giving a variation of from one half to one twentyfifth the original intensity of the phosphorescent gas. The entire apparatus is operated electrically, time being registered on a chronograph.

By means of this photometer the law of the rate of decay of phosphorescence for gases has been found; in this case, for air at from 0.1 to 0.4 mm. gas pressure, the expression is the same as that for the decay of phosphorescent solids, found by Nichols and Merritt.<sup>1</sup>

$$I = \frac{1}{(a+bt)^2}$$

<sup>1</sup> PHYSICAL REVIEW, XXII., 5, May, 1906.



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If the reciprocal of the square roots of the intensities are plotted with the corresponding times, a straight line is obtained. The points representing the observation of one decay of the phosphorescent gas are sufficient to demonstrate the law as shown by the accompanying curves. These curves shown in Fig. 1 are at different gas pressures, other conditions being the same. It appears that the initial intensities of the glows diminish very rapidly with decreasing gas pressure. An application of the law to the fading of the light of a body of phosphorescent gas as great in size as a long enduring meteor train shows that the light of the selfluminous meteor train can be explained on the assumption that it is a gas phosphorescence, although the train may be visible for thirty minutes. A certain brightening of the sky around the radiant point at the time of meteor showers which has been called the "auroral light" is also explained by the application of the same law. In the latter case it is probable that the feeble phosphorescing of many trains has combined to give a pale glow in the region of the heavens through which the shower was taking place.

The determination of the law for the decay of the phosphoresence of air, greatly strengthens the hypothesis that the meteor train is a gas phosphorescence; and also, if the meteor train is the same as this gaseous afterglow which can be produced in the laboratory, then a phenomenon precisely similar to the "auroral light" referred to above should be expected at every great meteor shower.

# EXPERIMENTS WITH THE LIPPMANN COLOR PHOTOGRAPH.<sup>1</sup> By Herbert E. Ives.

THE colors in this process are due to reflection from laminæ of silver deposited in the loops of the standing wave system formed by reflection of the incident light by a mercury surface in contact with the transparent photographic film. Theoretically the purity of the reflected colors should increase with the thickness of the film. In practice very thin films are used because the laminæ are formed to but a short distance and the absorption of light by them makes but few effective. The reflected colors are far from pure. The necessity for using a mercury trough has always been a disadvantage of the process. The colors of natural objects have been difficult of reproduction because the standing wave system is

practicable to flow. By using other developers, such as hydroquinone, even action throughout the film results. If the developed image is then bleached with mercuric chloride a transparent deposit is obtained, and the reflected light consists of a spectrum band of only a few A.U. in width, the purity increasing with thickness of film.

A substitute for the mercury mirror has been found. Celluloid varnish is flowed on silvered glass; on drying the celluloid and silver strip off together, this flexible mirror is then laid on a wet Lippmann film and allowed to dry. Exposure is made as with ordinary dry plates, the celluloid stripped off and film developed.

Because of the difficulty experienced in securing photographs of natural objects an application of the process to three-color photography was tried. For this fairly pure spectrum colors are needed and the Lippmann film is eminently fitted to give them. Pictures are made similar to the Joly picture, — alternating lines of red, green and blue, secured by successive exposure behind a line-screen to monochromatic lights.

#### VARIATION OF THE PENETRATING RADIATION.<sup>1</sup>

#### BY W. W. STRONG.

A N electroscope of the Wilson type was placed in screens of water, iron and lead. It was found that the rate of leak in the vessel under these conditions was constant. The same electroscope unscreened, however, shows very considerable changes in the rate of leak. By covering the electroscope with a thin cap of blackened wood, the effects of easily absorbable external radiations are eliminated. Under these conditions one gets the effects of the so-called penetrating radiation and temperature only. Under these conditions if the rate of leak is at any time the same as for the electroscope screened with iron or lead, it indicates that the penetrating radiation is zero. A few results will now be given, the rate of leak being the average over the period of time indicated.

	Tir		-				Rate of Leak, Scale Divisions per Second.	Per Cent. Penetrating Radiation.
1908, March 26,	ð	hrs	. 50	min.	. А.	м.		
	5	""	20	"	Ρ.	М.	.000014	40
March 27,	8	"			Α.	М.	.000016	60
	5	"	40	"	P.	М.	.0000155	55
March 28,	10	66	5	"	A.	М.	.000013	30
Showers,	5	"	5	"	Р.	M.	.000010	0
March 29,	2	"	25	"	Р.	М.	.000011	10
April 4,	8	"	15	"	Α.	М.		
-			••		T		*****	-

During March 28 there were showers. In general it has been found that during rains or snows the penetrating radiation is much smaller than usual. On April 3 the weather changed from being warm to being very cold. Under these cyclonic conditions of the winds, air from the colder and upper strata of the atmosphere flows towards the surface. It was found in this case that the penetrating radiation was practically of zero value. This would indicate that this air contained very little radioactive material — at least very little of the products that are the sources of penetrating  $\gamma$  rays.

JOHNS HOPKINS UNIVERSITY.

THE SPECIFIC HEAT OF SOME CALCIUM CHLORIDE SOLUTIONS.<sup>1</sup>

#### BY H. C. DICKINSON AND E. F. MUELLER.

A DETERMINATION of the specific heat of some calcium chloride solutions was first undertaken chiefly in the interests of the refrigeration industry to which it is of considerable importance.

A calorimeter of the continuous flow type was designed with a view to working at temperatures as low as  $-35^{\circ}$  C. and making determinations of specific heat in a temperature interval of from  $5^{\circ}$  to  $10^{\circ}$  with an accuracy of approximately 0.1 per cent. The calorimeter consists of a heavy copper vessel of about one liter capacity containing some two meters of copper tubing wound with resistance wire and bent into a spiral, a second coil of resistance wire and a stirrer. Since it was not necessary to know the water equivalent with accuracy, kerosene was used for filling, with the heating coils directly immersed in it.

A stream of calcium chloride brine from a cold reservoir is drawn through the copper coil under a constant head and the temperature of the calorimeter maintained constant by supplying energy electrically. The use of two heating coils, one of which is in close contact with the brine coil and the other separated from it, makes it possible to choose within rather wide limits all the temperature conditions and the rate of flow, by adjusting the ratio of energy supplied by the two coils. The calorimeter proper is held within a larger closed vessel by heat-insulating supports and kept at the same constant temperature as this vessel by observing a differential thermo-couple. By this method radiation and conduction and water equivalent corrections are almost negligible. The energy supplied by the stirrer is determined by separate experiments at different speeds.

Measurements to be taken are as follows: (1) Time (usually ten minute intervals) observed on a carefully regulated watch, (2) weight of brine, (3) energy supplied electrically, by potentiometer with standard

<sup>1</sup>Abstract of a paper presented at the Washington meeting of the Physical Society, April 24-25, 1908. shunt and volt box, (4) temperature difference between inlet and outlet of the brine coil, measured by differential platinum resistance thermometers (described in the June, 1907, PHYSICAL REVIEW), (5) inlet temperature of brine, measured by one of the resistance thermometers. The rate of stirring and small changes in the temperature of the calorimeter are also observed and corrections made, seldom amounting to one per cent. of the energy used.

The following results are only preliminary as the investigation is still in progress. Observations have been made on one of the purest and most generally used commercial calcium chlorides with results as follows, with a probable error not exceeding 0.1 per cent. unless possibly for the most dense brine at the lowest temperatures.

Specific	gravity	1.26	Specific	heat	.666 + .00064/	$(-35^{\circ} \text{ to } 15^{\circ})$
••	**	1.20		"	.708 + .00064/	(-20° " 15°)
	**	1.14	"	"	.772 + .00064/	(-10° " 15°)
" "	**	1.07		"	.869 + .00057/	( 0° " 15°)

A few determinations have also been made with pure water as a check on the method and the value found for the specific heat at 15 was .9995 with a negative correction for temperature but the magnitude of this correction was not carefully determined. These results are all reduced to a value of 4.196 for the  $15^{\circ}$  calorie in electrical units based on the international ohm and volt.

Absorption Spectrum of Neodymium in Mixed Solvents.<sup>1</sup>

BY JOHN A. ANDERSON.

**X** 7HEN pure, anhydrous neodymium chloride is dissolved in water it gives a very characteristic absorption spectrum for which Beer's law holds accurately unless the solution is nearly saturated. If the anhydrous salt is dissolved in methyl or ethyl alcohol or acetone the same statement is true, but the absorption spectrum is different from that of the aqueous solution, most of the bands having apparently shifted somewhat towards the longer wave-lengths in accordance with Kundt's law; also, the structure of the bands is generally different in different solvents. It was thought to be of interest to try the effect of using mixtures of water and one of the non-aqueous solvents, keeping the concentration of the dissolved substance constant but varying the proportion of one of the solvents to the other in the mixture. It was found that the spectrum of neodymium chloride does not change appreciably when the proportion of methyl or ethyl alcohol to water was varied from o to 85 per cent., and that when the proportion was varied from 85 per cent. to 100 per cent. there is not a gradual shift of the bands but that two

<sup>1</sup>Abstract of a paper presented at the Washington meeting of the Physical Society, April 24-25, 1908. sets of bands coexist; the bands characteristic of the aqueous solution disappearing gradually, while those due to the alcoholic solution increase in intensity.

The composition of the mixture in which the two sets of bands have about equal intensity for a half-normal solution was found to be roughly 8 per cent. water and 92 per cent. alcohol. For a quarter normal solution it was roughly 5 per cent. water and 95 per cent. alcohol. In both cases, therefore, the two sets of bands have equal intensity when the mixture contains about ten molecules of water to each molecule of neodymium chloride.

The results indicate that the absorption spectrum of the aqueous solution is due to some definite hydrate which is always formed provided there is sufficient water present. If the amount of water is not sufficient then some of the neodymium chloride will combine with the alcohol forming perhaps some definite alcoholate having an absorption spectrum different from that of the hydrate.

This work is a part of an investigation on the absorption spectra of solutions carried out during the present year by Professor H. C. Jones and the writer.

JOHNS HOPKINS UNIVERSITY, April 9, 1908.

Optical Properties of Colloidal Solutions and Turbid Media in the Infra-Red.<sup>1</sup>

# BY B. J. SPENCE.

A NUMBER of theoretical and experimental papers have appeared from time to time dealing with the optical properties of colloidal solutions and turbid media. Among the more recent are those of Müller,<sup>2</sup> whose paper is of an experimental nature, and the article of Mie<sup>3</sup> which is largely theoretical.

Among the earlier memoirs is one by Garnett,<sup>4</sup> which has an important bearing upon the investigation. The analysis given by Garnett was extended by the present writer, so that it is possible to make use of it by him in investigating the colloidal solutions.

In Garnett's analysis, he develops the following equation :

$$\epsilon' = \pi'(1 - K') = 1 + \frac{3M\frac{H^2 - 1}{H^2 + 2}}{1 - M\frac{H^2 - 1}{H^2 + 1}}$$



where n' = refractive index of the colloidal solution,

K' = absorption coefficient of the colloidal solution,

M = volume of metal per c.c. of supporting medium,

$$H = n(1 - iK),$$

n =refractive index of the metal,

K = absorption coefficient of the metal.

In the above analysis it is assumed that the metallic particles are spherical in shape and that there are many to the wave-length.

The work of Ehrenhaft<sup>1</sup> and Zsigmondy and Siedentopf,<sup>3</sup> has shown that these suspended particles are spherical in shape and of the order of magnitude of  $10^{-6}$  cm. One important theory in Garnett's work is the fact that the optical properties seem to be independent of the number of particles in unit volume.

Garnett's analysis was so developed as to account for an absorbing supporting medium and to give value for the optical constant n of the metals. The equations are the following:

$$n^{3} = \frac{4\beta(v^{3}A - v^{3}gK) + (2v^{3}gA + 3v^{3}K)}{2\beta(A^{3} + 4K^{3}g) - (Ag + 4K^{3}g)} - \sqrt{\left\{\frac{4\beta(v^{3}A - v^{3}gK) + (2v^{3}gH + 3v^{3}K)}{2\beta(A^{3} + 4K^{3}g - (Ag + 4K^{3}g))}\right\}^{2}} - \frac{2v^{4}(g + 2\beta)}{\beta(A^{3} + 4K^{3}) - (Ag + 4K^{3}g)}$$

where

$$\beta = \frac{-g}{3^{\mu}} + \sqrt{\frac{g^2}{9^{\mu^2}} + \frac{{n'}^2 K'^3}{9^{\mu^2 \nu^2}}}$$

and  $\nu =$  refractive index of the supporting medium,

g = absorption coefficient of the supporting medium,  $A = K^2 - 1$ .

The general deduction from these equations is, first, the absorption of the colloidal solutions is directly proportional to the relative volume  $\mu$ , or the concentration; second, that the value of n is independent of the supporting medium, n being what is usually defined as the refractive index of the metals.

The work was performed with a large spectro-bolometer provided with a rock salt prism 16 cm. in height and a face width of about 5.5 cm. The colloidal solutions were electrically prepared, both in water and ethyl malonate.

The values of  $\pi$  for gold, silver, and platinum lie upon a smooth dispersion curve, and were carried to a wave-length of  $20 \times 10^{-5}$  cm. The range of values is somewhat limited due to the strong absorption of water and ethyl malonate after it reaches a wave-length of  $19 \times 10^{-5}$  cm. A typical turbid medium composed of non-conducting particles was made of gum mastic and its properties studied. It showed an increased transparency for the longer wave-lengths as did the colloidal solutions. The absorption was found not to vary directly as the concentration, but as some other linear function. It remains yet to investigte whether turbid media (composed of non-conducting particles) obey the Rayleigh formulas, where the energy transmitted varies as the  $\lambda^{-4}$ .

The above is submitted as a preliminary report of work which is still in progress, and nearing its completion.

# THE EFFECT OF WAVE FORM UPON MAGNETIC HYSTERESIS.<sup>1</sup>

#### BY MORTON G. LLOYD.

MANY previous workers have sought to measure the energy expended in hysteresis with different frequencies and different forms of wave, but with results in such disagreement that the question may be considered as unsettled as yet. The author, with Mr. J. V. S. Fisher, has made measurements of the total iron losses with alternating magnetization by plotting curves between the instantaneous values of magnetizing current and magnetic flux. The apparatus used for this purpose has been described in a paper already published.<sup>2</sup>

The loops so obtained represent the total energy due to both hysteresis and eddy currents, and the value of the hysteresis alone cannot be accurately determined.

The wattmeter method has consequently been used to measure the total iron losses, and a separation of the hysteresis and eddy current components effected by using two frequencies and applying the modified form of the Steinmetz formula

# $W = anB^a + bn^3B^3f^3$

where W is the power expended, n the frequency, B the maximum value of the flux density, a and b constants of the material, and f the form factor of the electromotive force induced in a coil enclosing the flux. The form factor is measured by means of the apparatus described in the

<sup>1</sup>Abstract of a paper presented at the Washington meeting of the Physical Society, April 24-25, 1908.

<sup>2</sup> Lloyd and Fisher, Bull. Bureau of Standards, 4, p. 467, 1908.



article cited above, which also serves to determine the shape of the wave of magnetic flux and to fix the value of the maximum flux density. The form factor is altered by introducing resistance in the magnetizing circuit, or by introducing the third harmonic into the E.M.F. by means of a special set of generators. The change in eddy current loss with form factor can be computed, and the change in total loss is measured. If these are not equal, there must also be a change in hysteresis. The samples experimented upon were in the form of rings, made up by using sheet iron or iron wire. The results show that if there be any change in the hysteresis, with change of wave form, when B is kept constant, it is very small.

# Additional Observations on the Selective Reflection of Salts on Oxygen Acids.<sup>1</sup>

#### BY LEIGHTON B. MORSE.

I N a previous paper<sup>a</sup> it was shown that in general the bands of selective reflection, three and only three of which were found between  $4 \mu$  and  $15 \mu$  in each of eight simple carbonates with bivalent bases, shifted toward longer wave-lengths as the atomic weight of the base was increased, and further that this displacement was roughly proportional to the change in the atomic weight of the base.

The data obtainable on the first reflection bands of simple nitrates and sulphates were in agreement with the carbonates. Only crystalline solids free from water of crystallization, with simple elements as bases, were considered and salts having bases with the same valence as the acid radical were selected.

Since we know that the positions of reflection bands in salts of a given acid are influenced by the atomic weight of the base, when comparing the wave-lengths of bands of selective reflection characteristic of the different acid radicals it is necessary to eliminate as far as possible the effect of the base. The nearest approach to this was obtained by selecting salts of potassium for the monovalent acids and of calcium for the bivalent acids (atomic weight K = 39.15, Ca = 40.1).

At the time of writing the previous paper only carbonates had been examined, but combining the writer's data on  $CaCO_{s}$  with the data of other observers<sup>3</sup> on KNO<sub>s</sub>, CaSO<sub>4</sub>, and MgSiO<sub>5</sub> (there were no data on CaSiO<sub>5</sub> and MgSiO<sub>5</sub> was the best substitute obtainable), it was found that an approximate linear relation existed between the wave-lengths of the first with a given weight of oxygen (48 grams was taken as in the carbonates). Making allowance for magnesium being lighter than calcium, it seemed that the approximate linear relation found could hardly be accidental. The tentative hypothesis was made "that the oxygen atom is the one chiefly responsible for the marked reflection observed."

A number of salts with oxygen acid radicals were examined which, if the supposed linear relation held, might be expected to give bands corresponding to the first band in carbonates, in the region of the spectrum for which a rock salt prism is transparent. Thus the reflection of one or more salts of ten different oxygen acids have been examined between  $4\mu$ and 15 µ including CaCO<sub>2</sub>, KNO<sub>2</sub>, AgNO<sub>3</sub>, CaSO<sub>4</sub>, KClO<sub>4</sub>, CaSiO<sub>2</sub>, KClO<sub>2</sub>, PbCrO<sub>4</sub>, KMnO<sub>4</sub>, and CaTiO<sub>2</sub>. Nine of these have a weight of the acid-forming element less than the weight of the oxygen with which it is combined and without exception the potassium and calcium salts have their first bands at wave-lengths not only in the order of the weights combined with a given weight of oxygen, but the relation between the wave-length of the band and the weight of the acid-forming element combined with 48 grams of oxygen is roughly a linear one. The reflection curves of AgNO, and PbCrO, indicate that KNO, and CaCrO, which could not be directly examined because the former is highly deliquescent and the latter contains water of crystallization, have bands not far from the line drawn through the first bands of the other potassium and calcium salts.

Wollastonite,  $CaSiO_{s}$ , has a first band at the calculated wave-length 9.2  $\mu$  and beside this has a broad complex band toward the long waves from the first, but not far enough to fit in with the second region band found in the carbonates and found now for the first time in potassium and silver nitrates and in calcium sulphate. In perovskite,  $CaTiO_{s}$ , we have the largest weight combined with the given weight of oxygen in the acid radical (atomic weight Ti = 48.1,  $O_{s} = 48$ ). Its first band lies further toward the long waves than was predicted.

The values found for the wave-lengths of the first reflection bands had in most cases been calculated to within a few per cent. The second bands found in CaCO<sub>3</sub>, KNO<sub>3</sub>, and CaSO<sub>4</sub> seem to be related to each other. The AgNO<sub>3</sub> surface showed a low broad first band and it was impossible to determine whether or not the second band was present. The prediction of the second band in the other substances was beyond the sulphate band found at 14.5 +  $\mu$  and could not be found, if present, with the rock salt prism used.

The substances examined include salts of all the common monobasic

general formula  $M\overline{AO}_n$ . It must be kept<sup>1</sup> clearly in mind however that present data do not form any reasonable basis for assuming that all the reflection bands in even the simpler oxygen acids are connected with each other by such a simple relation as that found to hold roughly for the first bands, and which may be found to hold also for the second bands in the salts examined.

NEW GROUPS OF RESIDUAL RAYS IN THE LONG-WAVE SPECTRUM.<sup>2</sup>

BY E. F. NICHOLS AND WM. S. DAY.

THE apparatus used consisted of a number of Nernst glowers, usually five, as the source of radiation, a fine wire transmission grating, a reflecting spectrometer, and a Nichols radiometer, all enclosed in a glass case from which water-vapor was excluded. The mean wave-length of the residual rays after five successive reflections from polished rocksalt surfaces wa smeasured and found to be  $\lambda = 52.3 \mu$ , somewhat larger than  $51.2 \mu$  found in 1898 by Rubens and Aschkinass. Residual rays were also found after five successive reflections from polished surfaces of the following substances, the wave-length of maximum energy in the diffraction spectrum of the first order being given in each case :

Ammonium chloride,	$\lambda = 51.4 \mu$
Witherite (barium carbonate),	$\lambda = 46.5 \mu$
Strontianite (strontium carbonate),	$\lambda = 43.2 \mu$

As the radiometer had a thin quartz window, these wave-lengths are subject to revision because the changing transparency of quartz in this part of the spectrum would tend to shift the maximum energy observed to the long-wave side.

It should be noticed that the wave-lengths of the three known groups of residual rays from chlorides — potassium chloride, sodium chloride, and ammonium chloride,  $61.1 \mu$ ,  $52.3 \mu$ ,  $51.4 \mu$ , while not strictly proportional, lie in the order of the atomic weights of their respective bases, 38.8, 22.9, 18. The same rule holds for the residual rays from the carbonates of barium and strontium, the heavier base giving the longer wave-length.

Note on the Radioactivity of Ordinary Metals and on the Penetrating Radiation from the Earth.<sup>2</sup>

By J. C. MCLENNAN.

**T**N a paper in the Phil. Mag., December, 1907, the writer described

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made of lead, of zinc, and of aluminium. With the zinc and aluminium cylinders carefully cleaned, a conductivity was obtained for the enclosed air, which on reduction gave the value 15 for q, the number of ions generated in the air per c.c. per second.

With lead cylinders which were investigated more extensively than those of other metals, the conductivity exhibited wide variations, and values were obtained which ranged from 160 to 23 ions per c.c. per second.

During the past eight months experiments on the conductivity of air confined in metallic vessels have been continued in the Physical Laboratory at Toronto by Mr. C. S. Wright, and he has now obtained under normal conditions with a particular lead cylinder of the dimensions given above, a conductivity corresponding to the production of 15.3 ions per c.c. per second. With zinc and aluminium cylinders the lowest conductivities obtained by him as yet give respectively the values 13.4 and 12.5 ions per c.c. per second for q.

With gamma rays of the same intensity from radium traversing in turn the three cylinders of lead, zinc, and aluminium, which gave the values for q of 15.3, 13.4 and 12.5 respectively, the relative values of the impressed conductivities were found to be 14.00, 11.4 and 10.00. These relative values, it may be added, were found to be the same with gamma rays of all intensities. From the difference exhibited between these relative values and the numbers found for q for these same cylinders, it is clear that the whole of the conductivities obtained with them under normal conditions cannot be ascribed to a penetrating radiation existing at the surface of the earth and to a secondary radiation excited by it at the walls of the receivers.

With a view to ascertaining what portion of the conductivity obtained with each cylinder could be ascribed to the penetrating radiation and to the secondary radiation excited by it, a series of measurements was made on the conductivity of the air in the three cylinders in and about the neighborhood of Toronto. The results of these measurements are recorded in the following table.

The numbers obtained for q at station 2 it will be seen appear to be the lowest hitherto recorded under any circumstances for the ionization of air in closed vessels measured at normal pressure and temperature.

The average value obtained for q with the lead cylinder in the experiments over the surface of the water of Lake Ontario, as the table shows, was 9 ions per c.c. per second. The difference between this number and that obtained at station 10 in the laboratory, viz., 6.3 ions per c.c. per second, would therefore correspond to the conductivity impressed upon the air by a penetrating radiation which was present in the laboratory and by the secondary radiation necessarily accompanying it, but

which was entirely absent from the space in the open above the surface of the lake. The water of the lake would then appear to act as a screen for a penetrating radiation issuing from the earth. Some investigators, notably Strong, Phys. Zeit., February 15, 1908, have suggested that the atmosphere was the source of the penetrating radiation known to exist at the surface of the earth, but these results, coupled with the values obtained for the ionization at Station 8 on the University tower, constitute strong evidence against the validity of that view.

# TABLE I.

	Observation Station.	Remarks.	Value of $q$ , the Number of Ions Generated per c.c. per Second.				
No.	Location.		Lead.	Zinc.	Aluminium.		
1.	The ice on Toronto Bay, 100 meters from the Yacht Club Wharf.	Water, 10 meters deep. Ice, 30 cm. thick.	90				
2.	The ice near Canoe Club Wharf, Toronto Bay.	Water, 5.6 meters deep. Ice, 30 cm. thick.	8.6	6.0	6.55		
3.	The ice on Grenadier Pond, an inlet of Lake Ontario. Station "a."	Water, 2.5 meters deep. Ice, 30 cm. thick.	9.2				
4.	The ice on Grenadier Pond. Station "b."	Water, 3.5 meters deep. Ice, 30 cm. thick.	9.0				
5.	At the shore of Grena- dier Pond. Station "c."		9.1				
6.	On a sand hill overlook- ing Grenadier Pond.	Height of hill about 50 meters. Distance from shore, 100 meters.	9.3				
7.	University lawn.	Clay soil, sodded, frozen and covered with ice and snow, 20 cm. deep.	11.2				
8.	University tower.	26 meters high.	11.4				
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#### Table of Conductivities.

Confirmative evidence of the existence of this difference in the conductivities of air when contained in a closed vessel measured on land and on the surface of the water of Lake Ontario was obtained in some measurements made in September last. In that month, a series of observations was made in the laboratory on the conductivity of air in a lead cylinder, and the average value for q with this receiver was found to be 41.7 ions per c.c. per second. Measurements were also made with this same receiver on board the steamer "Corona" during one of her passages over Lake Ontario, and an average value for of 35.8 ions per c.c. per second was found. A third set of measurements was then made on land in the open on the south side of the lake at a number of points between Oueenston and Niagara Falls, and an average value of 42.6 was found for q. Here again it will be seen that a difference of approximately 6 ions existed between the values found for q on the water and those found for this quantity on the land. It is interesting to note in this connection that very little variation was obtained in the conductivity in the measurements made at different points during the passage of the boat, although the depth of the water at the wharf was only some 6 meters, while at the middle of the lake it was over 150 meters deep.

The experiments made at Stations 5 and 6 are also of special interest, as the conductivity obtained at these points was practically the same as that obtained in the experiments on the surface of the lake, which shows that the sand was entirely free from the radioactive substances which were probably present in the clays and rocks at other points of observation. Some additional evidence of this freedom from radioactive substances was obtained from a further set of observations made in December last at Ward's Island, which is a low-lying sand bar forming part of the boundary of Toronto Bay. There the conductivity of air in a lead cylinder was found to be the same when measured on the island as when measured on the water of the adjoining bay.

Some years ago the writer made an examination of the water of Lake Ontario and was unable to detect in it any measurable amount of radium emanation. From the lack of emanation in this water, and from the uniformity existing in the values obtained for q on its surface for all depths, it would appear probable that the water entirely cuts off any radiation coming from the soil or rocks beneath it.

In support of this view some experiments made on the absorption by this water of the gamma rays from radium may be cited.

A capsule containing thirty milligrams of radium was hermetically sealed in a glass tube which was then enclosed in a tube of brass whose walls were 1 cm. in thickness. This tube was then laid on the ice on Grenadier Pond, and the ionization cylinder supported on a table 113 cm. high was placed over it, and the conductivity due to the radium measured. A hole was then made in the ice and the tube containing the radium lowered to different depths, the ionization in the cylinder at each depth being measured. The values found for Q the number of ions generated per c.c. per second by the radiation from the radium for the various depths are given in Table II.

# TABLE II.

Depth of Over Tube Cont	Q	
0 m	eters.	4,485.0
0.5	"	447.2
1	•4	16.11
2	"	.69
3.65	"	.62

From this it will be seen, after allowing for a variation in the intensity of the radiation due to the increased distance from the measuring chamber, that the intensity of the radiation reaching the ionization cylinder after traversing 3.65 meters of water, was not more than one part in 500 of its intensity when the radium was on the surface of the ice. From these numbers it would appear, therefore, that if the water of the lake contributed itself no penetrating radiation, the amount which could get through the water to the surface from the earth beneath would form a negligible proportion of that issuing from the different rock and soil surfaces on land.

On the basis of this argument it follows that the ionizations given in Table I. for observation Station 2 may be taken to represent the conductivities impressed upon the air either by intrinsic radiations issuing from the metals of the receivers themselves, or else by radiations from active impurities still remaining in them.

The difference between the numbers for this station and those for station 10 are, as will be seen from the table for the different cylinders, as follows: Lead, 6.7; zinc, 7.4; aluminium, 5.95. These numbers, as is evident, are not proportional to the relative ionizations impressed on the air in the three cylinders by the penetrating rays from radium. The number for zinc, especially, exhibits a considerable discrepancy, and further measurements should be made to ascertain the cause of it.

Considered as a whole the experiments described above are interesting from the light which they throw on the question of radioactivity of metals and substances generally. The values obtained for q for the three cylinders at Station 2 differ from each other but little. They are moreover of

of almost any metal selected at random. Considering also the difference in the atomic weights of the three substances, aluminium, zinc, and lead, and having in mind that radioactivity is a property associated with atomic structure, it would seem that if these metals could be obtaired entirely free from active impurities, and the conductivity of air contained in vessels made from them studied, it would be found, if the observations were carried out under conditions or in places where no ionization was possible from penetrating radiations arising from external sources, to drop to a very low value if it did not entirely vanish.

The experiments described in this note were made with one of C. T. R. Wilson's latest type of gold-leaf electrometers, which was found, on account of its portability, and of the facility and exactness with which readings could be made with it, to be most admirably suited to the purposes of the investigation.

PHYSICAL LABORATORY, UNIVERSITY OF TORONTO, March 30, 1908.

# THE INFLUENCE OF TERMINAL APPARATUS ON TELEPHONIC TRANSMISSION.<sup>1</sup>

BY LOUIS COHEN.

THE problem of telephonic transmission has been very ably treated by several investigators. One has to examine only the collected papers of Dr. Oliver Heaviside, and the two papers on the "Propagation of Electrical Waves" by Professor M. I. Pupin, and he will find a discussion on almost every phase of the problem. But while there is very little that one could add to the mathematical treatment of the problem, yet there is one point in connection with this problem "The Influence of Terminal Apparatus on Telephonic Transmission" which has not been given sufficient attention, and I trust a brief discussion of this phase of the problem will be of some interest.

If L, R, C denote the inductance, resistance and capacity of the line per unit length; X the current, V the potential at any point on the line, then the equation of propagation will be as follows:

$$L\frac{d^3x}{dt^3} + R\frac{dx}{dt} = \frac{1}{c}\frac{d^3x}{ds^3}$$

At the terminals the following relations will obtain

$$V_{i} = X_{i} \left\{ R_{1} + i \left( L_{1}p - \frac{\mathbf{I}}{C_{1}p} \right) \right\},$$
$$V_{0} = Ee^{ipi} - X_{0} \left\{ R_{0} + i \left( L_{0}p - \frac{\mathbf{I}}{C_{0}p} \right) \right\},$$

where  $R_1$ ,  $L_1$ ,  $C_1$ , and  $R_0$ ,  $L_0$ ,  $C_0$  are the resistance, inductance, and capacity of the receiving and sending instrument respectively.

From the above equations we can obtain the most general expressions for the current and potential at any point on the line which are as follows:

$$\begin{split} X &= \frac{E c p}{2 \sqrt{K_1^2 + K_2^2}} \left\{ e^{\left[\beta \xi \cos\left(pt - a\xi + \theta\right) + e^{-\beta \xi} \cos\left(pt + a\xi + \theta\right)\right]} \\ &+ \sqrt{H_1^2 + F_1^2} \left[ e^{-\beta \xi} \cos\left(pt - a\xi - \varphi + \theta\right) - e^{\beta \xi} \cos\left(pt - a\xi - \varphi + \theta\right] \right\}, \\ V &= \frac{E \sqrt{a^2 + \beta^2}}{2 \sqrt{K_1^2 + K_2^2}} \left\{ e^{-\beta \xi} \left[ \cos(pt + a\xi + \theta + \omega) - e^{-\beta \xi} \cos(pt - a\xi + \theta + \omega) \right], \\ &+ \sqrt{H_1^2 + F_1^2} \left[ e^{\beta \xi} \cos(pt - a\xi - \varphi + \theta + \omega) + e^{-\beta \xi} \cos(pt + a\xi - \varphi + \theta + \omega) \right] \right\}, \end{split}$$

where

$$a = \sqrt{\frac{1}{2}} \sqrt{cp} \{ \sqrt{P^{2}L^{2} + R^{2}} + pL \}, \quad \beta = \sqrt{\frac{1}{2}} \sqrt{cp} \{ \sqrt{P^{2}L^{2}} + \overline{R^{2}} - pL \},$$

$$\tan \theta = \frac{K_{1}}{K_{2}}, \quad \tan \varphi = \frac{H_{1}}{F_{1}}, \quad \tan \omega = \frac{\beta}{a}, \quad \xi = l - s,$$

$$H_{1} = \frac{Cp}{a^{2} + \beta^{2}} \left\{ -a \left( L_{1}p - \frac{I}{C_{1}p} \right) + \beta R_{1} \right\},$$

$$F_{1} = \frac{Cp}{a^{2} + \beta^{2}} \left\{ \beta \left( L_{1}p - \frac{I}{C_{1}p} \right) + aR_{1} \right\},$$

$$H_{1}^{2} + F_{1}^{2} = \frac{C^{2}p^{2}}{a^{2} + \beta^{2}} \left\{ \left( L_{1}p - \frac{I}{C_{1}p} \right)^{2} + R_{1}^{2} \right\}.$$

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$$K_{2} = \frac{e^{\beta l} + e^{-\beta l}}{2} \left\{ -\beta \sin al + C\rho R_{1} \cos al \right\}$$
$$+ \frac{e^{\beta l} - e^{-\beta l}}{2} \left\{ a \cos al - C\rho \left( L_{1}\rho - \frac{I}{C_{1}\rho} \right) \sin al \right\}$$

Taking account of the sending apparatus makes the expressions for  $K_1$  and  $K_2$  much more complicated, and they are given in the complete paper which will soon be published.

When s = l, that is at the receiving end of the line, we have

$$X_{i} = \frac{Ecp}{\sqrt{K_{1}^{2} + K_{1}^{2}}} \cos{(pt - \theta)},$$
$$W_{i} = \frac{Ecp}{\sqrt{\left(L_{1}p - \frac{1}{C_{1}p}\right)^{2} + R_{1}^{2}}}{\sqrt{K_{1}^{2} + K_{1}^{2}}} \cos{(pt - \varphi - \theta - \omega)}.$$

In calculating the value of  $X_i$  as given by the above equation I have assumed three distinct cases: (1) The terminal apparatus neglected entirely, (2) the receiver included in circuit, and (3) the receiver in series with a condenser in circuit.

I have assumed three distinct frequencies, 500, 1,000 and 1,500, and two different lines, one 30 km. long and one 300 km. long.

The constants of 30 km. line (Cable, 19 B. S.) are approximately as follows:

$$L = .00001$$
 henry per km.,  
 $C = 0.045$  microfarad,  
 $R = 27.5$  ohms.

Using these constants and assuming that the impressed voltage corresponding to the frequencies 500, 1,000, 1,500, are  $E_1$ ,  $E_3$ ,  $E_5$  respectively, we shall have the following table.

	Frequency = 500.	Frequency = 1,000.	Frequency = 1,500.
Case 1, no terminal apparatus. Case 2, receiver in circuit. Case 3, receiver and a conden- ser of 1.5 m.f. in circuit.	$X_l = 0.00176E_1$	$X_l = 0.005 E_3$	$     X_l = 0.00089E_{\delta}      X_l = 0.0046E_{\delta}      X_l = 0.0045E_{\delta} $

An examination of the above table shows that the receiver in the circuit increases the distortion, and it is further seen that the introduction of a condenser will improve the transmission.

Now while telephoning at such short distance is possible with almost any apparatus, yet it will be admitted that there is considerable room for improvement, and it would seem that the introduction of a condenser of the proper magnitude in series with the receiver ought to produce good results.

To show the effect on the distortion in long distance transmission, I have made similar calculations for a cable (13 B. S.) 300 km. long. The electrical constants of such a cable are approximately as follows:

L = 0.0001 henry per km., C = 0.045 microfarad per km., R = 7 ohms per km.

Using these values and the constants of the receiver the same as in the previous case, we get the the following table :

	Frequency = 500.	Frequency = 1,000.	Frequency = 1,500.
Case 1, no terminal apparatus. Case 2, receiver in circuit.	$X_{i} = 0.003E_{1}$ $X_{i} = 0.00126E_{1}$ $X_{i} = 0.0014E_{1}$	$X_i = 0.00011E_s$ $X_i = 0.00017E_s$	$X_i = 0.000053E_s$ $X_i = 0.000045E_s$ $X_i = 0.000045E_s$
Case 3, receiver and a conden- ser of 1.5 m.f. in circuit.	$X_l = 0.0014E_1$	$X_l = 0.0002E_s$	$X_l = 0.00005 E_s$

From the table it can be seen that the introduction of the telephone receiver does not materially influence telephonic transmission.

# An Electrodless Method for Measuring the Conductivity of Electrolytes.<sup>1</sup>

## BY LOUIS COHEN.

IF we insert a tube filled with an electrolyte into a solenoid, and then pass an alternating current through the winding of the solenoid, eddy currents will be generated in the electrolyte which will heat the electrolyte and thus consume a certain amount of energy.

Let us suppose now that the solenoid forms one arm of a Wheatstone bridge, through which we pass a high frequency current, and let us determine its resistance with and without the electrolytic core, there evidently will be a difference in the two measurements, for the loss of energy in the electrolyte due to the eddy currents will effect the measurement as if an additional resistance was inserted in that arm of the bridge. Now it is quite evident that the energy loss in the electrolyte will be proportional to its conductivity, hence the change in resistance measured in the bridge will be proportional to the conductivity of the electrolyte

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I have worked out the mathematics of the problem and I find the following relation obtains:

$$R = 2\pi^{*}\lambda p^{*}n^{*}la^{*},$$
$$\lambda = \frac{R}{2\pi^{3}p^{3}n^{3}la^{4}},$$

where R denotes the increase in resistance (measured),

p denotes  $2\pi \times$  frequency,

*n* denotes number of turns per cm.,

/ denotes length of electrolytic core,

a denotes radius of electrolytic core.

As to the magnitude of the quantity R, we can readily see from the following example. Suppose  $\lambda = 10^{-9}$ ,  $p = 2\pi \times 10^4$ , n = 10, l = 50 cm., a = 7 cm. Then  $R = (2\pi^3 \times 10^{-9} \times 4\pi^3 10^8 \times 10^2 \times 50 \times (\overline{49})^3/10^9)$  = 3 ohms approximately. The resistance of the winding of the solenoid calculated by the formula given in my paper<sup>1</sup> "The Influence of Frequency on the Resistance and Inductance of Solenoidal Coils" is found to be about 55 ohms. The change in resistance will therefore be about six per cent., of sufficient magnitude to be determined with considerable accuracy.

WHAT IS THE MOST IMPORTANT PORTION OF A THERMOELEMENT.<sup>2</sup>

BY WALTER P. WHITE.

A LONG a thermoelement as ordinarily used, there are three temperature regions; one, fairly constant, at each end, and an intermediate gradient region where the temperature changes from one of the end values to the other. (In an element used with a cold junction in ice, there are usually two such temperature systems in series.) The present paper applies only where this temperature distribution exists. In such cases, applying the formula for electromotive force of a thermoelement which is not perfectly homogeneous,

$$E = \int \theta dH$$

( $\theta$ , temperature, H, thermoelectric power, E, electromotive force), it is easy to show that, except for second order corrections: (1) the temper-

This conclusion is little more than an extension of the well-known rule that solder or other foreign material at the junction affects the electromotive force but little. Nevertheless, it seems worth stating, both on account of its importance and because much in the literature seems to point to a very different conclusion and to emphasize the importance of the (usually) really unimportant portion of the thermoelement near the junction.

The following practical conclusions follow :

1. In selecting wire for a thermoelement, the gradient portion is the only part where great care needs to be exercised. The production of a good thermoelement is thus easier than has sometimes appeared.

2. If an inhomogeneous element is shifted to a different depth in the bath or furnace, it (in general) at once becomes a different element. The effect of a change in the material near the junction, however, is much less important.

3. In amputating a contaminated platinum thermoelement to restore its original value, it is usually practically sufficient to cut off only enough so that fresh uncontaminated wire occupies the gradient region.

Commercial constantan wire has been obtained whose original variations in thermoelectric power were 0.001 of the electromotive force against copper. By suitable selection and combination of this wire, thermopiles were easily constructed good to one part in one hundred thousand, that is, .001 of a degree at 100°. These even showed no variation in reading equal to .001 of a degree when the depth of immersion in a constant temperature bath at 100°, and therefore the position of the gradient region, was varied several centimeters.

## SPECIFIC HEATS AT HIGH TEMPERATURES.<sup>1</sup>

## BY WALTER P. WHITE.

THE substances under examination were dropped from an electric resistance furnace into the calorimeter described a year ago. The errors of the calorimeter were negligible. The loss of heat in the air was eliminated by first determining the heat given out by an empty platinum crucible at various temperatures and then subtracting this as an empirical correction from the total heat of crucible and included material. The empty crucible was weighted with platinum so as to keep constant conditions with regard to the splash, etc. The total loss of heat of the crucible alone (and this includes also the slight loss from the formation of steam as the crucible strikes the water) was only 4 per cent. The crucible was dropped electrically (Harker's method) by melting a supporting wire. This was done automatically by the swinging aside of a shield between furnace and calorimeter. The principal source of error (1 per cent. or more) was found in the uncertain tem-

<sup>1</sup> Abstract of a paper presented at the Washington meeting of the Physical Society, April 24-25, 1908.

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perature distribution within the furnace; a longer and narrower furnace is expected to diminish this. The accidental errors averaged about .3 per cent., that is, duplicate results usually agreed as well as this.

# THE APPLICATION OF THE IONIZATION FROM HOT BODIES TO THERMOMETRIC WORK AT HIGH TEMPERATURES.<sup>1</sup>

### BY O. W. RICHARDSON.

THE paper directs attention to the possibilities of the phenomena exhibited by the emission of ions by hot bodies for the determination of high temperatures in the absolute scale. Two methods of attacking this problem are outlined, which are independent of one another as regards their theoretical foundations. The theoretical and practical advantage of the two methods are discussed.

# **Resonance Spectra of Sodium Vapor.**<sup>1</sup>

### BY R. W. WOOD.

**CODIUM** vapor has a banded absorption spectrum comprised between  $\mathbf{N}$  wave-lengths 4,500 and 5,700 and extending from wave-length 580 far out into the infra-red, probably to 15 or  $20 \mu$ . There are between five and six thousand lines in the banded spectrum in the blue-green region. If the non-luminous vapor of the metal, contained in a steel tube is illuminated with white light, it emits a brilliant green light (fluorescent) which appears to be the exact compliment of the absorption spectrum. If, however, monochromatic light is thrown into the vapor, the spectrum of the emitted light consists of isolated bright lines, separated by intervals of about 38 Ångström units. In many cases the wave-length interval is remarkably constant, not varying by more than one or two tenths of a unit. If we excite the vapor with the light of the magnesium arc (green triplet "b") the emission spectrum of the vapor shows the triplet repeated a number of times at regular intervals. Since bright line spectra obtained in this way appear to be radically different from spectra obtained by any other means, I propose that they be designated resonance spectra, since they are without doubt the result of resonance vibrations set up within the molecule by the absorption of light of a single periodicity. Similar spectra have been obtained with the vapor of potassium, and probably other metallic vapors will show the phenomenon as soon as we learn how to handle them. Excitation of the sodium vapor with the light of the lithium arc gives a beautiful series of lines in the red and orange region as well as in the green and blue (slide shown). During the past winter these resonance spectra have been photographed over again with a con-

<sup>1</sup> Abstract of a paper presented at the Washington meeting of the Physical Society, April 24-25, 1908.

cave grating of 14 feet radius, which enables us to determine the wavelengths of the bright lines in the series to within 0.1 A.U. This work has been done in collaboration with Mr. Felix Hackett, fellow of the Royal University of Ireland.

The apparent absence of polarization in the light emitted when the vapor is excited by white light has always appeared to me to be difficult to reconcile with the theory that the radiation is directly reëmitted by the resonating electrons. On making a more critical examination I have recently found that in a direction making an angle of 90° with that of the exciting beam, the fluorescent light is partially polarized, even when the exciting light is unpolarized. The amount of polarization is about 15 per cent, when the incident light is unpolarized and 30 per cent. when a polarized excitation is used. It is clear that the vibrations in the exciting light which are parallel to the direction in which the fluorescent light is emitted, will, on the most elementary theory of the phenomenon which we can form, excite a vibration which cannot send out transverse waves in the direction specified. In other words the electrons will be moving in the line of sight. Or putting it in another way, if the electrons are free to move in any direction, the incident beam cannot excite vibration parallel to the direction in which it is travelling. On this theory we should expect complete polarization of the reëmitted light. That only about 15 per cent. is polarized can perhaps be explained by assuming that we are dealing with constrained motion. If an electron could only vibrate along a straight line the position of which within the molecule was fixed, vibrations would occur for all positions of the line except one (parallel to the incident beam) and these vibrations would in general have a component parallel to the incident beam. It is also possible that rotation of the molecules and collisions with neighboring molecules may exert a depolarizing action. The matter is under investigation at the present time. The presence of 11 per cent. of polarized light in the solar corona makes a fluorescence theory of the corona plausible.

INTERFERENCE OF LIGHT IN CHLORATE OF POTASH LAMINÆ.<sup>1</sup>

### By R. W. WOOD.

CRYSTAL plates have been obtained which reflect metallically a band in the spectrum less than 15 Ångström units in width, or less than three times the distance between the D lines. Photographs of the spectrum of the light transmitted through the crystal, showing the corresponding dark band were shown. Such crystals must contain six or seven hundred parallel twin planes only half a wave-length apart.

<sup>1</sup>Abstract of a paper presented at the Washington meeting of the Physical Society, April 24-25, 1908.



## ON DIFFUSE REFLECTION OF INFRA-RED ENERGY.<sup>1</sup>

## BY A. TROWBRIDGE.

A STUDY of reflection from powders of transparent materials to size of the particle being of the same order of magnitude as the wavelength of the reflected energy.

Powders of fluorite, sylvite, rock salt and sulphur show a slight increase in diffuse reflection with increasing wave-length.

Powdered quartz shows marked "body colors" in the region where the crystal shows only slight absorption and a marked "surface color" in the region where the crystal begins to absorb strongly.

## THE INFRA-RED ABSORPTION AND REFLECTION OF COLLODION.<sup>1</sup>

## By A. TROWBRIDGE.

A STUDY of the optical properties of collodion undertaken with the object of determining whether it would prove a suitable substance with which to coat rock salt surfaces in order to preserve polished surfaces.

The extinction coefficient of collodion is practically negligible in the region between the visible spectrum and  $\lambda = 6 \mu$ . In this region a rock salt plate or prism is more transparent when coated with a thin film of collodion than it is without being coated.

In the region from  $6 \mu$  to  $10 \mu$  there are two narrow absorption bands and one extended region of absorption for all of which the extinction coefficient attains values great enough to cause well-marked surface color.

# THE ABSORPTION AND REFLECTION OF CALCITE AND ARAGONITE FOR INFRA-RED RAYS AS DEPENDENT UPON THE PLANE OF POLARIZATION.<sup>1</sup>

BY R. E. NYSWANDER.

CLEAR polished crystal sections, cut to contain the principal directions of vibration, were investigated with polarized light for absorption and reflection. A Nernst heater furnished the source of energy which was polarized by reflection from a smooth selenium surface. A reflecting spectrometer employing the method of constant angle of emergence was used. Energy was measured with a radiometer. Reflecting power was compared with that of silver, which was assumed total.

The absorption band in calcite at  $11.3 \mu$  was found to be due to complete absorption of the extraordinary ray, the ordinary ray showing no trace of an absorption band in this region. The band at  $14.1 \mu$  occurs in both rays, but to a small extent in the extraordinary ray, while for the

<sup>1</sup>Abstract of a paper presented at the Washington meeting of the Physical Society, April 24-25, 1908. ordinary ray absorption is complete. Bands of metallic reflection are present at both of these points.

The reflection from aragonite as dependent upon the plane of polarization for the three principal directions of vibration shows that the band of metallic reflection at  $11.55 \mu$  is due to the reflection of one ray, and for this ray the reflection is nearly equal to that of silver. The two other directions of vibration show no increase in reflecting power through this region. In the region of  $14.1 \mu$  reflection bands are present for each direction of vibration. The direction showing the smallest reflecting power between  $11 \mu$  and  $12 \mu$  reflects most copiously at the second band, reflecting 29 per cent. of the incident energy. Two of these bands occur at  $14.1 \mu$ , the other is shifted to  $14.2 \mu$ .

# A Study of Photo-Electric Cells Containing a Fluorescent Electrolyte.<sup>1</sup>

## By PERCY HODGE.

THE above mentioned cells have been investigated by the writer in three different series of experiments. The original object of the work was to determine whether there is a change of conductivity of a fluorescent solution when under the influence of the exciting light. The solutions used were both dilute and concentrated, the solvent being absolute alcohol. The exciting light was an arc lamp, and the resistance measurements were made with an ordinary Wheatstone's bridge and galvanometer, as being more sensitive than any of the alternating current apparatus used for measuring resistances of solutions. The conclusion arrived at was that in the cells investigated, if the electrodes are entirely concealed from the light, or if the liquid is kept rapidly moving past the electrodes, no change is produced as great as 0.1 per cent. when the liquid is illuminated.

The second stage in the experiments was an investigation of the effect of illuminating anode and kathode in turn, changing the potential difference at the terminals of the cell from 0.2 volt, by small stages up to 3.6 volts. Very large changes in apparent resistance were observed when the potential differences were small, the effect at kathode being to greatly decrease the resistance, that at anode to increase it in about the same amount. As the potential differences became greater these effects became less, and finally the effect on the kathode became an increase of resistance and that at anode a decrease. Of these latter effects that at kathode was much the greater. Finally both effects were lost at about 3.5 volts.

The last work which has been done grew out of results of the last ex-

<sup>1</sup>Abstract of a paper presented at the Washington meeting of the Physical Society, April 24-25, 1908.

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periments, and has been a study of photo-active effects produced by illuminating one electrode only, no external electromotive force being applied. This effect, in the case of a number of fluorescent substances which have strong absorbing power, has been found quite large, the electromotive force produced reaching a maximum of between two and three tenths of a volt, near the infra edge of the absorption band, falling off abruptly as the electrode leaves the absorption band on the infra side, and much more gradually toward the violet. In all cases thus far observed when alcoholic solutions were used the exposed electrode became positive to the unexposed. One cell has been tried with fluorescein in water solution as the electrolyte, in which the effect was of opposite sign. The writer expects to publish in a short time a more extended account of his work, in which curves will be included to illustrate the above phenomena.

# The Principles Involved in the Selection and Definition of the Fundamental Electrical Units to be Proposed for International Adoption.<sup>1</sup>

## BY F. A. WOLFF.

IN the paper the work of the next International Electrical Congress was briefly outlined. Especial stress was laid on the question of the choice of the fundamental units as will be seen from the summary of the conclusions which follow:

1. The decisions of the Berlin Conference of 1905 should not be regarded as binding in view of the large amount of work since published on the silver coulometer and standard cell.

2. The international electrical units to be adopted should be regarded as separate and distinct from the absolute units on which they were originally based.

3. The choice between the ampere and the volt should be made exclusively on the basis of merit.

4. That the principles on which the decision should be made are

a. Accuracy of reproduction from specifications.

b. Concreteness.

c. Ease of reproduction.

5. The accuracy of reproduction of the coulometer remains to be established, as coulometer measurements made by different investigators establish only relative accuracy, no accurate comparisons of the results obtained by different investigators having thus far been made.

6. If a decision must be at the present time and on the basis of merit, the cell should be selected on account of the advantages it offers from the

<sup>4</sup>Abstract of a paper presented at the Washington meeting of the Physical Society, April 24-25, 1908. standpoint of concreteness and ease of reproduction, since no greater accuracy of reproduction can be claimed for the coulometer in the light of the data at hand. In addition this choice is more logical from the standpoint of the standardizing laboratory as it leads to fundamental units corresponding to the standards submitted for certification as well as corresponding to the methed employed for measuring currents in terms of standards of resistance and electromotive force.

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7. In view of the preference indicated for the coulometer at the Berlin Conference, the reproducibility of the cell and coulometer should, however, first be definitely established by systematic international coöperation, which would also result in bringing to light unrecognized defects in the specifications proposed.

8. If the ampere is defined in terms of the coulometer, the value to be taken for the standard cell and which must be depended on between coulometer measurements, must be determined at each of the national standardizing institutions, the results obtained reduced to a common basis by exchange of cells and resistance standards, and a mean value taken to insure international uniformity.

Unless the accuracy of the result, involving errors in the realization of both the ohm and ampere is greater than that attainable in the reproduction of the cell from specifications, the definition of the ampere will subsequently be ignored, making the cell in effect a primary standard. The same result can be more directly obtained by selecting the volt as the second fundamental unit since a practically equivalent value may be assigned to the cell, in which case the corresponding value for the electrochemical equivalent of silver need not be known to the highest accuracy, as it could only be used for the purpose of loosely defining the ampere.

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## NEW BOOKS.

## NEW BOOKS.

Vorlesungen über theoretische Spektroscopie. Von A. GARBASSO. Pp. viii + 256. Barth, Leipzig, 1906.

Professor Garbasso's book emphasizes in the most striking way the ground that has been traversed in this important department of optics within the last decade. The thirty years which followed the great work of Bunsen and Kirchhoff were spent chiefly in the accumulation of experimental data and the bewildering wealth of material amassed testifies to the industry and enthusiasm of the army of spectroscopists who entered the new domain.

This series of lectures deals with the explanation of those portions of optics, such as anomalous dispersion, selective absorption, surface color, optical resonance, the occurrence of spectral series and of double and triple lines, the Zeeman effect, etc., which lay beyond the range of the older theories. The explanation has its foundation in the electro-magnetic theory, into the terms of which the Helmholtz theory is translated. From the author's experiments on electro-magnetic resonance to the work of Rubens, E. F. Nichols and Aschkinass and thence to optical resonance in the visible spectrum, the steps are obvious. After the development of these relations the author proceeds in the later and more important chapters to the consideration of the behavior of various combinations of pendulums and from this he leads up to the construction of models corresponding to the molecules of complex compounds and to a general mechanical theory of the phenomena of radiation.

E. L. N.

Lehrbuch der Experimentalphysik. By ADOLPH WÜLLNER. Band 1. Allgemeine Physik und Akustik. 6th Edition. Revised by A. Wüllner and A. Hagenbach. 8vo. Pp. xiv + 1058. Leipzig, B. G. Teubner, 1907.

It is a pleasure to note the appearance of a new edition of this valuable reference book. The first volume, covering the field of General Physics and Acoustics, has been revised so as to include the more recent work up to the beginning of the year 1907. References to original articles are numerous and a complete index makes it easy to look up any particular topic.

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At the present time there appears to be no work in English which is to be regarded as the equivalent of the general treatises like that of Wüllner which have appeared in Germany and France. When one considers the enormous amount of work involved in the preparation of such a work it is not surprising that no one has been found to carry out the task. It is to be hoped, however, that an English translation of one of these general treatises may some time be undertaken, for it is unfortunate that so useful a book should not be available for all workers in physics in this country instead of for those only who are familiar with German.

E. M.

A Laboratory Guide for Students in Physical Sciences. By H. SCHAPPER. Pp. v + 61. New York, John Wiley & Sons, 1908.

The purpose of this little volume is explained by the following extract from the preface: "The student of physics cannot handle the results of his measurements in the laboratory and has no conception of the accuracy of his work without a course in precision of measurements. Between the meager information usually given on the subject in laboratory manuals and elaborate treatises on the adjustment of observations there is a considerable gap. This text-book is intended to fill the lacuna."

The book contains chapters on Units and Dimensions, Discussion of Results and Graphical Representation, Approximation Formulæ, Adjustment of Observations, Effect of Errors of Observation on the Result, and similar topics.

Mathematical Handbook containing the Chief Formulas of Algebra, Trigonometry, Circular and Hyperbolic Functions, Differential and Integral Calculus, and Analytical Geometry, together with Mathematical Tables. By EDWIN P. SEAVER. Pp. viii + 179. New York, McGraw Publishing Company, 1907.

This is a well selected and carefully arranged collection of formulas and tables which should be extremely useful to physicists, engineers and mathematicians. It is only by extended use that the full value of such a handbook can be ascertained and appreciated; but a small acquaintance with the book is sufficient to show that those who use it will have a growing appreciation of their indebtedness to the author for its compilation.

Alternating Current Motors. By A. S. MCALLISTER. Second edition. Pp. xi + 291. New York, McGraw Publishing Co., 1907.

At no too frequent intervals a book appears which is a distinct contribution to knowledge, on account of the original material it contains and the soundness of its treatment. Such a book is the one in hand which treats in a thorough manner the various types of alternating current motors. The reader is supposed to have a general knowledge of alternating currents. An occasional blemish is the involved sentence at times indulged in. This appears in parts of the book taken without sufficient revision from earlier papers by the author, and not at all in the new matter of the second edition. In an excess of effort to avoid ambiguity, the author has overworked such expressions as *time-phase* and *electrical-space-quadrature* in places where *phase*, *space-quadrature*, etc., would be sufficient.

Besides minor changes, the second edition contains a discussion of the interesting motor-converter, a chapter on leakage reactance and a well written supplement on the synchronous motor. This last is, we believe, the best discussion there is of the synchronous motor. A system of circular loci is developed, somewhat analogous to the circle locus for the induction motor, making possible a treatment both simple and adequate.

# Electrical Energy; its Generation, Transmission and Utilization. By E. J. BERG. Pp. xi + 184. New York, McGraw Publishing Co., 1908.

This, like the foregoing, is an authoritative book. Very nearly all the theory of polyphase alternating current is introduced and elucidated with reference to one concrete problem, namely, to transmit certain power, a certain distance for certain purposes. As applied to this problem, the author discusses inductance and capacity, both distributed and localized, skin effect, corona, resonance, wave form and harmonics, transformers, alternators, etc. The treatment is vivid for the theory is applied in every case to the problem at hand. B.

# An Introduction to the Study of Electrical Engineering. By HENRY H. NORRIS. Pp. 404. New York, John Wiley & Sons, 1907.

This book is entirely descriptive, written from the point of view that a student should have a knowledge of things and phenomena before any reasons can be ascribed to them. The writer states in the preface that electrical engineering is not a separate profession but is becoming more and more a component part of mechanical engineering, and the book is written from this standpoint. The book gives the student an introductory knowledge of the whole field of electrical engineering; it is assumed that more specialized knowledge will be gained in subsequent courses.

The writer has succeeded admirably in dealing with the side of the subject which he has selected.

# Electric and Magnetic Measurements and Measuring Instruments.

By FRANK W. ROLLER. Pp. v + 398. New York, McGraw Publishing Co., 1907.

This book is useful for laboratory reference; it is not adapted as a text book and it is doubtful if, outside of the laboratory, it will be of use to many engineers. Its real value lies in its full description of instruments, historic and modern; the description of methods is less satisfactory being often inadequate and without reference to original sources.

Laboratory Work in Electrical Engineering, Preliminary Grade. By JOHN ROBERTS, JR. Pp. x + 218. New York, D. Van Nostrand Company, 1906.

The scope of this book is partly in the field of electrical (physical) measurement and partly in the field of electrical engineering; and for some places, as the laboratory for which it was written, it may be well suited. For other places it may be found not to cover sufficiently either field. The chapter headings are: Graphical Representation of Experimental Results, Verification of Ohm's Law, Measurement of Resistance, Measurement of E.M.F., Measurement of Current, The Potentiometer, Calibration of Electrial Measuring Instruments, Miscellaneous Experiments.

Under miscellancous, are twenty-eight experiments in electrical engineering, which appears to be too much "preliminary," considering that they are all elementary and a wide field including all of alternating currents is still uncovered. It will seem to many that engineering students should devote their attention to experiments involving fundamental principles on the one hand and engineering methods on the other, without spending too much time on intermediate ground.

## Standard Handbook for Electrical Engineers. By a Staff of Specialists. Pp. xx + 1283. New York, McGraw Publishing Co., 1908.

The material of this book is the best of its class; the mechanical workmanship the worst. Type, illustrations and press work are poor, giving the appearance of the *n*th edition from hand-me-down plates. This is the more unfortunate on account of the great value of the subject-matter; the reviewer finds he must keep a copy on his desk and refers to it daily. The various sections covering the whole field of electrical engineering are prepared by specialists and contain a wealth of material; a great deal of this is new in a book of this kind and not quickly found even in a good library. Particularly is this true of alternating current transmission and apparatus. The arrangement and indexing is good and the different parts of the book are well harmonized. As the treatment of many subjects is necessarily brief, a reference in each case to an authoritative book or article would add enormously to the value of such a handbook. **B**.

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# Abhandlungen über Theoretische Physik. Band I, Erste und zweite Lieferung. By H. A. LORENTZ. Leipzig, Teubner, 1907. 8vo, pp. 489.

The author has taken advantage of the opportunity afforded by the republication of his papers in collected form to revise the form of presentation to some extent, and to introduce greater unity in the mathematical treatment and use of symbols. The papers have been arranged with reference to the subjects treated, and with little regard to their chronological order. Thus we find first a discussion of "The Principles of Dynamics," suggested by Hertz's "Prinzipien der Dynamik," and first published in 1902; after this two articles on "Die Bewegung einer reibenden Flüssigkeit," and "Die Entstehung turbulenter Flüssigkeitsbewegungen," which appeared in 1896-7; and next a paper on "Les Equations du Mouvement des Gaz et la propagation du son suivant la théorie cinétique des gaz," dated 1881. The use of either one of three languages, no one of them his own, apparently with equal facility, and certainly with a style that is always clear and pleasing, is something that will fill most American readers with envy.

The first part of the present volume is devoted to questions connected with dynamics and thermodynamics. In addition to the papers referred to above mention may be made of papers on Boltzmann's Virial theorem, on the Entropy of a Gas, the Second Law of Thermodynamics, the Molecular Theory of Dilute Solutions, the Distribution of Kinetic Energy among the Molecules of a Gas; and, as an illustration of the field covered, a paper on "Die Grösse von Gebieten in einer *n*-faction Mannigfaltigkeit."

The second part of the first volume contains two articles on crystal symmetry and the bounding surfaces of crystals. This section is however chiefly devoted to problems connected with optics and to papers dealing with the problem of the relative motion of the earth through the ether. The following titles may, for example, be cited: "Stokes' Theory of Aberration"; "Die Fortpflanzung des Lichtes in einem sich bewegunden Medium"; "Sur la méthode du miroir tournant pour la détermination de la vitesse de la lumiére"; "Die relative Bewegung der Erde und des Aethers."

It will be noticed that the papers contained in this first volume refer to numerous questions that have recently been the subject of very interesting discussions. The delightfully clear and illuminating manner in which such questions are treated by Professor Lorentz makes these papers invaluable to the specialist and extremely interesting to the general physicist. E. M. Lehrbuch der Thermodynamik in ihrer Anwendung auf das Gleichgewicht von Systemen mit gasförmig-flüssigen Phasen. Erster Teil. By J. D. VAN DER WAALS. Erster Teil. Bearbeitet von Dr. Ph. Kohlstamm. 8vo, pp. xii + 287. Leipzig and Amsterdam, Maas and Van Suchtelen, 1908.

The main title of Professor van der Waal's work is misleading in that it suggests a general treatise on Thermodynamics, whereas in reality no attempt is made in the book to cover the whole field. On the other hand the subtitle, which apparently restricts the discussion to the application of thermodynamics to systems containing liquid and gaseous phases, is perhaps even more misleading, since it implies a narrowness of scope that is not justified either by the list of topics given in the table of contents or by the method of treatment in individual cases.

The book is based upon lectures delivered by Professor Van der Waals at the University of Amsterdam and has been prepared for the press by one of his former students, Dr. Kohlstamm. The treatment is naturally more complete in those branches of the subject to whose development the author's own investigations have contributed. Thus the equation of state which bears the author's name is used in place of the equation of an ideal gas more frequently than is common in books on thermodynamics; and the thermodynamic theory of capillarity is given more than usual prominence. The fact that an authoritative and connected account is given of the author's important work in the domain of thermodynamics makes the book of especial interest and value. The subject of thermodynamics is one of such peculiar difficulty and has so many widely differing aspects that it seems impossible for one who is not himself an investigator in this field to prepare a satisfactory treatise on the subject. But a treatise written by a specialist is almost of necessity more or less one sided. Compare for example the three or four treatises on thermodynamics by the leading workers in this field. No one would call these works narrow; and the term one-sided also does not seem wholly appropriate. But the point of view and methods of treatment are so widely different that it sometimes seems as though there was nothing but a skeleton in common. In thermodynamics, more than in any other branch of physics, it is necessary to consult a number of different authorities in order to obtain a broad view of the subject. The addition of Professor Van der Waal's lectures to the list of treatises available for this purpose is a subject for congratulation.

The present volume is divided into four sections entitled respectively: "Der erste Hauptsatz und seine Anwendungen"; "Der Zweite Hauptsatz und seine Anwendungen"; "Das Allgemeine Gleichgewichtsprinzip und seine Anwendungen"; "Thermodynamische Theorie der Kapillarität." A second volume is to appear later. E. M. The Study of Stellar Evolution. An Account of Some Recent Methods of Astrophysical Research. By GEO. E. HALE. 8vo, pp. xi + 252 and 104 plates. Decennial Publications of the University of Chicago. University of Chicago Press, 1908.

The plan and scope of this very interesting book will be best explained perhaps by the following extracts from the preface :

"As first planned, this book was intended to serve as a handbook to the Yerkes Observatory. Many inquiries regarding the observatory's work, made by the numerous visitors received there annually, seemed to call for a printed explanation of the purposes in view and the observational methods employed. Removal to California and new duties connected with the organization of the Mount Wilson Solar Observatory caused a modification of the project. I finally adopted the plan of describing a connected series of investigations, laying special stress on the observational methods employed, in the hope of explaining clearly how the problem of stellar evolution is studied. The advantage of using concrete illustrations drawn, in large part, from personal experience, and the desire that the book should be of special service to visitors at the Yerkes and Mount Wilson Observatories, are sufficient reasons, I trust, for the otherwise undue proportion of space devoted to these institutions."

"I have made no attempt to deal with the general problem of stellar evolution, or to offer anything approaching an adequate description of the observational methods of astrophysics. The various researches described are chosen rather arbitrarily, in some cases with more regard for my personal acquaintance with the facts than because of their intrinsic importance. I trust, however, that although this method of treatment has necessarily resulted in a fragmentary exposition of the subject, the book will serve to show how the problem of stellar evolution is attacked along converging lines, leading from solar, stellar, and laboratory investigations."

The book is one that does not require great technical familiarity, either with astronomy or with physics, and may be put in the hands of one having only a general knowledge of these subjects with the certainty that by far the greater part of the book can be read with interest and understanding. For the physicist, however, and especially for one who has had experience with the difficulties and the charm of the experimental side of his subject the book possesses a fascination that is quite unusual. The author writes of problems to whose solution he has himself made important contributions, of instruments which he has designed, or of investigations with which, owing to his acquaintance with other astrophysicists, he has a thorough personal familiarity. This fact, together with the pleasing style and complete absence of any trace of egotism, gives to the book a character and charm that are rarely met with.

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The book contains at the end over one hundred full page plates, in all cases excellent photographic reproductions. Views of observatories are given, and of particular pieces of apparatus; numerous photographs of the sun, of prominences, sun spots, and flocculi; excellent photographs of star clusters and nebulæ; and an extended series of spectra illustrating the employment of spectroscopic methods in astrophysics. One photograph, which I have not before seen reproduced, gives a portrait of Rowland standing near his famous ruling engine. Several views of the Mount Wilson Solar Observatory and of the surrounding mountains are of great interest and beauty. E. M.

Theorie, Konstruction und Gebrauch der feineren Hebelwage. By Dr. W. FELGENTRAEGER. 8vo, pp. vi + 310. Leipzig and Berlin, Teubner, 1907.

The theory of the balance and the conditions to be met in the design of the different parts are discussed in great detail and by one whose experience in this field has been unusually extensive. The work is well illustrated by explanatory diagrams and by numerous photographs of complete balances and of individual parts. While the whole work will prove of the greatest value to the specialist the general physicist will probably be chiefly interested in the description of the types of balance that are suited for particular kinds of work and in the discussion of the proper conditions for their use.

Kleiner Leitfaden der praktischen Physik. 2d Edition. By F. KOHLRAUSCH. 8vo, pp. xviii + 268. Leipzig, Teubner, 1907.

Based upon the author's well known "Leitfaden der praktischen Physik," of which the present volume is an abbreviated edition, the book is intended for beginners in the laboratory, and especially for those who do not intend to specialize in physics. The appearance of a second edition indicates that it has been appreciated. In this country the language unfortunately prevents the use of the work as a text-book. But either this book or the original more complete "Leitfaden" is doubtless present as a reference book in almost every laboratory in the country.

Les Découvertes Modernes en Physique. By O. MANVILLE. Pp. 186. Paris, Libraire Scientifique A. Hermann, 1908. (Received.)

Immunochemistry. The Application of the Principles of Physical Chemistry to the Study of the Biological Antibodies. By SVANTE ARR-HENIUS. Pp. ix + 309. New York, The Macmillan Company, 1907. (Received.)

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# Die Milchstrasse. By MAX WOLF. 8vo, p. 48. Leipzig, Barth, 1908.

This pamphlet gives the text of an address by Professor Wolf before the Dresden meeting of the Naturforscher und Ärzte in 1907. It contains a description, popular in the best sense of the word, of the many interesting features of the Milky Way, illustrated by numerous excellent reproductions from photographs.



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